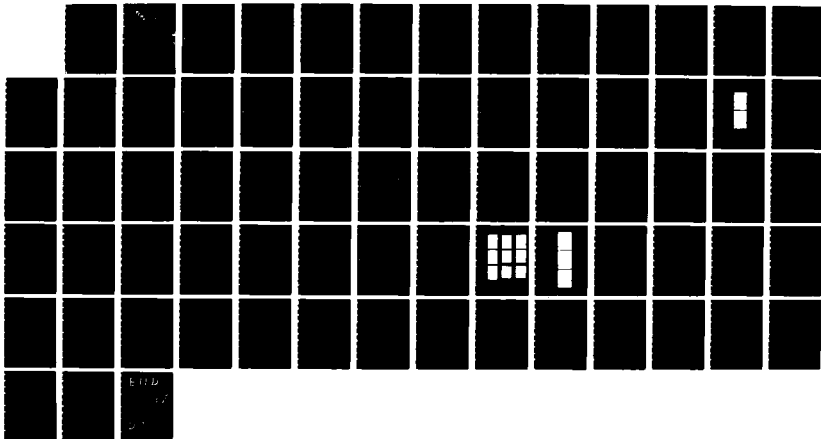


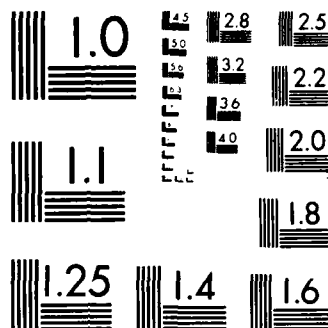
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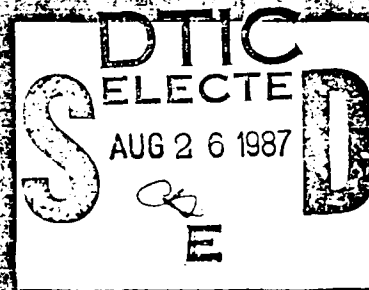
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Final Technical Report

on

High Pressure Strand Burn Rate Tests  
of Polyvinylnitrate/Nitramine Propellants



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Final Report PCRL-FR-87-004  
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Final Technical Report

on

High Pressure Strand Burn Rate Tests  
of Polyvinylnitrate/Nitramine Propellants

by

N.A. Messina, L.S. Ingram, G.F. Konig, and M. Summerfield

Submitted in fulfillment of  
Contract DAAA21-86-C-0067

Submitted to

U.S. Army AMCCOM, ARDEC  
ATTN: SMCAR-AEE-BR/P. Petrella  
Picatinny Arsenal, NJ 07806-5000

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Princeton Combustion Research Laboratories, Inc.  
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Director of Research

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SECURITY CLASSIFICATION OF THIS PAGE

## REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		1b. RESTRICTIVE MARKINGS NONE	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE		UNCLASSIFIED/UNLIMITED	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) PCRL-FR-87-004		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
6a. NAME OF PERFORMING ORGANIZATION Princeton Combustion Research Laboratories, Inc.	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION U.S. Army AMCCOM, ARDEC	
6c. ADDRESS (City, State and ZIP Code) 475 U.S. Highway One Monmouth Junction, NJ 08852		7b. ADDRESS (City, State and ZIP Code) ATTN: SMCAR-AEE-BR/P. Petrella Picatinny Arsenal, NJ 07806-5000	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION U.S. Army AMCCOM, ARDEC	8b. OFFICE SYMBOL (If applicable) SMCAR-AEE-BR	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER DAAA21-86-C-0067	
8c. ADDRESS (City, State and ZIP Code) Picatinny Arsenal, NJ 07806-5000		10. SOURCE OF FUNDING NOS.	
11. TITLE (Include Security Classification) High Pressure Strand Burn Rate Tests of Polyvinyl nitrate/Nitramine Propellants		PROGRAM ELEMENT NO.	PROJECT NO.
		TASK NO.	WORK UNIT NO.
12. PERSONAL AUTHOR(S) Neale A. Messina, Larry S. Ingram, Gustave F. Konig, and Martin Summerfield			
13a. TYPE OF REPORT FINAL	13b. TIME COVERED FROM 2/86 TO 12/86	14. DATE OF REPORT (Yr., Mo., Day) 10 JUNE 1987	15. PAGE COUNT 69
16. SUPPLEMENTARY NOTATION			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB. GR.	
19. ABSTRACT (Continue on reverse if necessary and identify by block number)			
<p>One approach to solving the problem of the erratic burning behavior, i.e., slope break, of nitramine gun propellants is to complex the nitramine propellant with polyvinyl nitrate (PVN) binder material, i.e., hydrogen bond the RDX or HMX with the unesterified hydroxyl groups in the binder. The objective of the current effort was to conduct independent high pressure strand burn rate tests of this new class of PVN/nitramine propellant, as distinct from high pressure closed bomb burn rate tests. Comparisons of strand burn rate data of solution processed PVN/nitramine "complexed" formulations with conventionally processed control formulations have been conducted. Also, comparisons of strand burn rate data and closed bomb burn rate data have been conducted.</p> <p>(Cont'd on following page)</p>			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS <input type="checkbox"/>		21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED	
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Neale A. Messina		22b. TELEPHONE NUMBER (Include Area Code) (609) 452-9200	22c. OFFICE SYMBOL

## SECURITY CLASSIFICATION OF THIS PAGE

The results of this study suggest potential ballistic performance improvements of the PVN/RDX propellants over state-of-the-art NC-base small caliber gun propellants. However, additional process improvements are needed to demonstrate the full potential for producing a complexed PVN/RDX gun propellant. The highly nitrated German PVN polymer demonstrated only limited capability for complexation of the nitramine. To assess the potential for complexing higher levels of nitramine, it is essential to examine less nitrated PVN. Also, the processing studies at Hercules, ABL indicated that the cure cycle is instrumental insofar as physical integrity of the extruded propellant grains is concerned. Adjustment of the cure cycle will modify residual solvent removal during processing, thereby affecting the degree of microporosity in the grains.

The most promising PVN/nitramine complexed formulation is Lot ISB 7803. No burn rate pressure exponent shifts are observed in the strand burn rate data and the standard deviation of the data at each pressure point is minimal. Complex Lot ISB 7803 offers significant improvements in propellant energy (impetus) and is a potential candidate for the family of low vulnerability (LOVA) propellants. Vulnerability testing including hot fragment conductive ignition tests (HFCIT) and full scale vulnerability tests are recommended. We are also of the opinion that a reduction of the PVN nitration level will result in further improvements of the vulnerability characteristics.

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## 1.0 Introduction

One approach to solving the problem of the erratic burning behavior, i.e., slope break, of nitramine propellants is to complex the nitramine propellant with the binder material, i.e., hydrogen bond the RDX or HMX with the unesterified hydroxyl groups in the binder. Work by Brodman of U.S. Army AMCCOM, ARDEC (Ref. 1 thru 3); Hercules, Allegany Ballistics Laboratory (Ref. 4), and others has included the study of hydrogen bonding between the nitro groups of 2,4 dinitrotoluene (a deterrent material) and unesterified hydroxyl groups in nitrocellulose, prepared in cast films. Free hydroxyl groups are available because cellulose used to make military grade nitrocellulose is not totally nitrated. Both the hydroxyl stretching region and the symmetric and non-symmetric nitro stretching regions were examined to characterize the hydrogen bonding properties in these previous researches.

Recent work at U.S. Army AMCCOM, ARDEC has indicated that a hydrogen bonded complex can also be formed between polyvinyl alcohol (PVA) and RDX. This was accomplished by preparing a solution of PVA and a solution of RDX, utilizing an appropriate mutual solvent. Appropriate quantities of the two solutions were mixed and thin films cast from the resulting mutual solution. After the solvent was evaporated, infrared spectroscopy of the films showed shifts in the OH group stretching frequency, indicative of hydrogen bond formation. The PVA used was actually polyvinyl acetate which had been hydrolyzed to approximately a 90% level. The remaining 10% acetate groups provided limited acetone solubility.

The ARDEC work is currently being continued under contract to Hercules, ABL, Contract DAAK10-85-C-0047 (Ref. 5). The study is focusing on examination of cast films as well as gun propellant. Propellant evaluation consists of analytical characterization and closed bomb burn rate characterization of "complexed" and conventionally processed control propellant formulations. Due to the indicated energy advantage of polyvinyl nitrate (PVN), experimental emphasis at Hercules, ABL has been shifted to this polymer rather than PVA.

Definitive conclusions from the analysis of closed bomb data conducted on Contract DAAK10-85-C-0047 were somewhat limited due to a combination of processing problems and grain porosity, both macroporosity and microporosity. Also questions were raised by Hercules, ABL during the process development phase of these PVN/nitramine gun propellants as to density of the propellant mixes and binder-solids bonding.

The objective of the current effort on Contract DAAA21-86-C-0067 was to conduct independent high pressure strand burn rate tests of this new class of PVN/nitramine propellant, as distinct from high pressure closed bomb burn rate tests. Comparisons of strand burn rate data of solution processed PVN/nitramine "complexed" formulations with conventionally processed control formulations have been conducted. Also, comparisons of strand burn rate data and closed bomb burn rate data have been conducted.



## 2.0 The PCRL High Pressure Strand Burner

PCRL has utilized its high pressure strand burner apparatus (275 MPa, 40,000 psi) for accurate and rapid determination of propellant burning rate. The primary observable during a test is the measurement of very small pressure excursions, which are a direct consequence of burning accurately machined short-length propellant strands in a hydraulic medium. From this observable the burning rate can be obtained. The major sub-assemblies of the high pressure apparatus include an air-actuated high pressure hydraulic pump, an accumulator, a liquid-filled (usually water) combustor cell, a specimen holder, and the pressure excursion data acquisition system (e.g., Kistler 607C4 piezoelectric pressure transducer and 504A charge amplifier).

The arrangement of the heavy-walled combustor, air-actuated high pressure hydraulic pump, and accumulator is shown in Figure 1. The heavy-walled combustor dimensions are shown in Figure 2. To prepare the propellant test specimens, an apparatus is available at PCRL to machine the specimens to a prescribed length and to insure that the top and bottom surfaces are parallel. The outer perimeter and the base of the strand are inhibited with a bituminous paint to eliminate all questions concerning flame spreading along the periphery. A flattened nichrome-wire igniter in zig-zag form is mounted on one end of the strand with a smear of cement to ignite the specimen.

The strand and its mount assembly are installed in the combustor which has been prefilled with water of controlled temperature and the system is pressurized to the desired test pressure. Previous studies by PCRL personnel have demonstrated that burning in a liquid medium does not affect burning rate for this particular experimental set-up.

The PCRL high pressure strand burner was used to generate baseline linear burn rate data for 0.200" diameter JA-2 propellant strands in the pressure range 5 kpsi to 40 kpsi. Three repeated tests at nominal pressures of 5, 7.5, 10, 12.5, 15, 20, 30, and 40 kpsi were conducted. The JA-2 propellant served as the "standard propellant" for baseline tests. Figure 3 illustrates the pressure excursion-time data recorded for the burning process of two repeated tests of single strands of JA-2 propellant in the PCRL high pressure strand burner with preset pressure of 40,000 psi. For Test 01, we see that for a strand length of 0.7995-in, the pressure excursion in the hydraulic pressurizing medium due to the burning process is 535 psig. Thus the mean pressure during the strand burn time is 40,268 psi. The measured burn time interval for Test 01 is 0.076 sec. Thus, propellant burn rate at the mean pressure of 40,268 psi is 10.520 in/sec. For Test 03, we see that for a strand length of 0.8030-in, the pressure excursion in the hydraulic pressurizing medium due to the burning process is 525 spig. Thus the mean pressure during the strand burn time is 40,263 psi. The measured burn time interval for Test 03 is 0.075 sec. Thus, propellant burn

rate at the mean pressure of 40,263 psi is 10.707 in/sec.

Tabular results for 0.200" diameter JA-2 strand burn rate as a function of pressurizing environment are given in the Appendix and are compared to strand burner tests conducted with 0.356" diameter JA-2 propellant on Contract DAAK11-84-C-0104. Since all propellant strands to be evaluated for the PVN/nitramine propellants were expected to be of nominal diameter 0.2", it was deemed necessary to demonstrate that the small strand diameter does not bias test results in the PCRL Strand Burner.

JA-2 strand burning rate data are plotted as  $\log r$  versus  $\log p$  for lot HCL85K003-001 (0.356" dia) and for lot HCL85K003-009 (0.200" dia) in Figure 4. Excellent agreement between the two sets of strand data is observed. Figure 5 displays a least squares linear fit to the data for each lot. The two linear plots are nearly indistinguishable. The JA-2 linear burn rate least squares linear fit may be expressed as:

for 0.356" strand diameter,

$$r = 0.0006615 p^{0.9101}$$

and for 0.200" strand diameter,

$$r = 0.0006304 p^{0.9167}$$

### 3.0 Discussion: High Pressure Strand Burn Rate Data

Table 1 presents the formulations of the PVN/nitramine propellants for which strand burner data were generated. The formulations generally fall into the following categories: control lots conventionally processed versus complex lots produced by the solution process, HMX lots versus RDX lots, and plasticized versus non-plasticized lots. A review of Table 1 indicates that the nitramine weight percentage in all formulations was nominally 75%. This high nitramine percentage was required in Hercules, ABL processing studies since PVN propellant containing less than 75% nitramine, although processable, is apparently too soft to cut with a small arms cutter. This high nitramine percentage in combination with the highly nitrated German PVN (95.37% N) utilized by Hercules, ABL resulted in only partial complexation of the nitramine based on available (unesterified) hydrogen bonding sites. Thus when we speak of complexed propellant we should bear in mind that this refers to partially complexed formulations in which there is a relatively low level of complexable nitramine and a high percentage of crystalline nitramine.

Lot ISB 7799 is a control lot of nominally 25/74 weight percent PVN/HMX conventionally processed with ethanol-acetone solvent. The initial HMX particle size is 4.56  $\mu$ . Lot ISB 7800 is a complexed propellant lot of nominally 25/74 weight percent PVN/HMX produced by the solution process with acetone as solvent. The initial HMX particle size is again 4.56  $\mu$ . Lot ISB 7801 is a complexed propellant lot of nominally 24.5/72.5 weight percent PVN/HMX similar to Lot ISB 7800 except with the addition of 2% dioctyladipate (DOA) plasticizer.

Lot ISB 7776 is a control lot of nominally 25/74 weight percent PVN/RDX conventionally processed with ethyl acetate solvent. Lot ISB 7797 is also a control lot of nominally 25/74 weight percent PVN/RDX conventionally processed but with acetone as the processing solvent. Lots ISB 7783 and 7802 are both complexed propellant lots of nominally 25/74 weight percent PVN/RDX produced by the solution process with acetone as solvent.

Lot ISB 7792 is a control lot quite similar to control Lot ISB 7797 except with the incorporation of approximately 2% by weight of DOA plasticizer. Lot ISB 7803 is a complexed propellant lot quite similar to complexed propellant Lot ISB 7802 except with the incorporation of approximately 2% by weight of DOA plasticizer.

The strand burn rate data obtained in the high pressure strand burner apparatus is now discussed, keeping in mind physical observations made by Hercules, ABL on strand integrity (porosity, binder/nitramine dewetting, presence of large crystalline nitramine particles) and density measurements. All tabular burn rate data are presented in the Appendix.

Strand burn rate data for Lot ISB 7799, the 25/74: PVN/HMX

Control, is shown in Figure 6. It is obvious that this control lot produces unacceptably high data scatter. The large data scatter is also evident in Hercules, ABL low pressure strand burn rate data at 2,500 psi, as shown in Figure 6 by the "I-beam" representing the  $\pm 1\sigma$  standard deviation of the ABL low pressure burn rate data. In fact, when different fractions of the lot were cured differently in an attempt to minimize strand porosity, entirely different low pressure burn rate behavior was observed, as evidenced by the two distinct "I-beams" at 2,500 psi. It is uncertain as to the fraction, 7799A or 7799B, that PCRL evaluated in its high pressure strand burner, but this is irrelevant. The data scatter is far too extreme for Lot ISB 7799 for it to be considered a viable candidate for a gun propellant.

The burn rate data for Lot ISB 7800, the 25/74: PVN/HMX complex, are shown in Figure 7. These data are more well-behaved although it may be argued that the data variation at each pressure point is still excessive and that better processing control is desirable. Photomicrographs taken by Hercules, ABL at 20X magnification show evenly dispersed voids, nitramine agglomerates, and large nitramine crystals in the strands. Evidently the large nitramine crystals arose from recrystallization that occurred as the residual acetone solvent was removed during processing. It should also be noted that, in the range of 5,000 to 40,000 psi, a single straight line fit can be used to represent the burn rate data. However, if the Hercules low pressure strand burn rate data at 2,500 psi are taken into account, a low pressure burn rate exponent shift may be present, at pressures less than 5,000 psi. The least squares linear fit to the data in the pressure range 5,000 - 40,000 psi is shown in Figure 8. A burn rate pressure exponent of 0.8433 is indicated.

The addition of 2% DOA plasticizer to the PVN/HMX complex propellant formulation did little to improve the reproducibility of the high pressure burn rate data. This is shown in the burn rate-pressure data of Figure 9 for Lot ISB 7801. Again a single straight line fit to the data in the pressure range 5,000 - 40,000 psi is appropriate, as seen in Figure 10. However, as was the case for Lot ISB 7800, if we take into account the Hercules low pressure burn rate data at 2,500 psi, a low pressure burn rate exponent shift may be present at pressures less than 5,000 psi.

It is instructive to look at the effect of DOA plasticizer on complex propellant burn rate. The individual data points at each pressure are shown in Figure 11 for Lot ISB 7800 (no plasticizer - open circles) and for Lot ISB 7801 (2% DOA plasticizer - filled-in circles). The least squares linear fit to each data set in the range of pressures from 5,000 psi to 40,000 psi is shown in Figure 12. The addition of 2% DOA plasticizer to the complexed PVN/HMX formulation reduced the measured burn rate slightly and increased the burn rate pressure exponent from 0.8433 to 0.9353. The slight reduction in burning rate over the pressure range with the addition of DOA plasticizer

is in keeping with the attendant decrease in energy of the formulation.

At this point we shift our focus to PVN/RDX formulations. Nominal compositions and actual compositions for these propellants are shown in Table 1. Two control lots with nominally 25/74 weight percent PVN/RDX were evaluated for high pressure burn rate characteristics. These are designated ISB 7776 and ISB 7797. The processing solvent for each control lot was different, ethyl acetate being used for ISB 7776 and acetone being used for ISB 7797. The burn rate data for control Lot ISB 7776 are shown in Figure 13. The burn rate variability at each pressure point is somewhat excessive. Interestingly no single straight line fit to the burn rate data over the pressure range is possible. A piecewise linear fit to the data is indicated in Figure 14, in which two distinct slope breaks exist, one at approximately 10 kpsi and the second at a higher pressure, approximately 20 kpsi. Attempts to reproduce this double slope break behavior for the PVN/RDX control propellant with the processing of Lot ISB 7797 with acetone as solvent led to unacceptable variations of the burn rate data. Large data scatter is observed in the results of Figure 15. The large data scatter is also evident in Hercules, ABL low pressure strand burn rate data at 2,500 psi, as shown in Figure 15.

The burn rate data for Lot ISB 7783, the 25/74: PVN/RDX complex are shown in Figure 16. The reproducibility of these data is quite good, except for the presence of two outliers at high pressures (25 kpsi and 40 kpsi). In the range of 5,000 - 40,000 psi a single straight line fit can be used to represent the burn rate data, as shown in Figure 17. A burn rate pressure exponent of 0.9878 is indicated. A comparative plot of the linear least squares fit to the burn rate data for this complexed propellant and its control is shown in Figure 14. This is our first indication that the solution process, producing partial complexation of the nitramine, alters the erratic burning behavior, i.e., slope break, of conventionally processed nitramine propellant. The slope breaks appear to have been eliminated.

Lot ISB 7802 was an attempt to reproduce the desirable burn rate characteristics of Lot ISB 7783. Both these lots are 25/74: PVN/RDX complexes utilizing acetone as the processing solvent. Unfortunately the reproducibility of the burn rate data for Lot ISB 7802 (Figure 18) is not as good as observed for Lot ISB 7783 (Figure 16). The reason for this observed lack of burn rate reproducibility for Lot ISB 7802 must lie in the processing procedures adopted by Hercules, ABL. It should be recalled that the processing solvent remained unchanged. Although not explicitly stated by Hercules, we assume that both of these complex propellant lots were made by dissolving all ingredients in acetone and then removing enough solvent during mixing to permit extrusion. We further assume that the RDX particle size for both lots is identical, 5.35  $\mu$ . The reason, therefore, may be that different cure cycles were adopted, which critically

affects strand porosity.

A linear least squares fit to the burn rate data for Lot ISB 7802 is shown in Figure 19. The burn rate pressure exponent is 0.8209. Figure 20 shows a comparison plot of the burn rate data for Lots ISB 7783 and 7802 and Figure 21 shows a comparison plot of the linear least squares fit to each data set.

The addition of nominally 2% DOA plasticizer to the PVN/RDX control propellant formulation did little to improve the reproducibility of the burn rate data. This is shown in the burn rate-pressure data of Figure 22 for Lot ISB 7792. The large data scatter is also evident in Hercules, ABL low pressure strand burn rate data at 2,500 psi. Photomicrographs taken by Hercules, ABL of Lot ISB 7792, prepared with acetone solvent with no attempt to dissolve the large particle RDX ( $12.3\mu$ ), indicate minimal voids, i.e., macropores, most likely attributable to the use of the DOA plasticizer. The poor burn rate reproducibility may be due to either microporosity or to poor binder-large particle nitramine binding.

Finally, high pressure burn rate tests were conducted with Lot ISB 7803, a nominally 24.5/72.5: PVN/RDX complex propellant produced by the solution process with acetone as the processing solvent and with 2% DOA plasticizer added to the formulation during processing. The measured burn rate data are shown in Figure 23. We observe excellent reproducibility of the burn rate data over the entire pressure range  $5 \leq p[\text{kpsi}] \leq 40$ . A least squares linear fit produces the relationship  $r = 0.0005727 p^{0.9334}$  (see Figure 24). No slope break is evident in the data. Commensurate with this observation of excellent reproducibility of burn rate data is the observation of consistently smooth pressure excursion waveforms up to the point of strand burn-out, approximately 400 psig over the imposed strand bomb hydraulic pressure in the pressure range from 5,000 to 40,000 psi, as shown in Figure 27. No anomalies or discontinuities in the pressure production rate of the pressure excursion waveforms are observed for Lot ISB 7803.

It is instructive to compare the burn rate data for Lot ISB 7802 with those of Lot ISB 7803, both being nominally 25/74: PVN/RDX formulations but with Lot ISB 7803 containing 2% DOA plasticizer. This is shown in Figure 25 with the linear least squares fit to each data set shown in Figure 26. The burn rate data for Lot ISB 7802 are uniformly higher than corresponding burn rate data for Lot ISB 7803 due to the incorporation of 2% DOA in the ISB 7803 formulation, i.e., Lot ISB 7803 is less energetic than Lot ISB 7802.

Table 2 summarizes the pressure exponent and coefficient for the least squares linear fit to each set of burn rate data, for those lots where excessive data scatter does not preclude the fit to the burn rate law  $r = ap^n$ .

#### 4.0 Summary: High Pressure Strand Burn Rate Data

In the majority of tests conducted with the end ignited cylindrical strands of PVN/nitramine complexed propellant in the PCRL high pressure strand burner, a smooth pressure excursion of approximately 400 psig over the imposed strand bomb hydraulic pressure was observed, even though Hercules, ABL SEM studies showed evidence of varying degrees of unconnected micropores. Examples of the recorded pressure excursion for complex propellant Lot ISB 7803 are shown in Figure 27, in which all strand burn rate tests in the range 5,000 to 40,000 psi gave smooth pressure excursion waveforms to the point of strand burn-out. For the majority of control lots of conventionally processed PVN/nitramine propellants, with or without use of plasticizing agent, an undesirable lack of reproducibility of burn rate data and high apparent strand burn rates were observed. In only one case of a control propellant lot, ISB 7776, was a reduced level of data scatter observed. Hercules, ABL SEM studies showed evidence of varying degrees of connected porosity (communicating channels) forming microcracks in these control lot propellant strands. The pressure excursions recorded for several strand burn rate tests of Control Lot ISB 7797, for instance, illustrate an anomolous waveform, i.e., pressure generation profile, as shown in Figure 28. A discontinuous rate of pressure production is observed, leading to large data scatter in deduced burning rates. Interestingly, for Lot ISB 7797, none of the pressure excursion data for hydraulic pressures greater than 20,000 psi display this type of p-t discontinuity. This phenomenon will be discussed in more detail in the next section.

In general, the partial complexation achieved by the solution process produced strands with evenly dispersed unconnected voids with pore size approximately 100-150 diameter as determined by Hercules SEM studies, and no microcracking. The porosity level was 15-20% as determined from Hercules mercury pycnometer density measurements. The solution process leads to more reproducible burn rates for all "complexed" lots. This solution process results in PVN/nitramine propellants whose burn rate behavior shows no slope break over the entire pressure range 5,000 - 40,000 psi, although if one takes into account Hercules low pressure strand data at 2,500 psi it may be argued that a low pressure burn rate exponent shift occurs in the vicinity of 5,000 psi. Also, there is some indication that the solution process eliminates the high pressure burn rate slope breaks observed for conventionally processed PVN/ nitramine propellant, but only two data sets confirm this behavior, Control Lot ISB 7776 and Complex Lot ISB 7783.

The most promising PVN/nitramine complexed formulation is Lot ISB 7803. We observe that a single straight line fits the burn rate data extremely well over the entire pressure range. The standard deviation of the burn rate data at each pressure point is minimal.

## 5.0 Combustion Characteristics of Porous Propellants

Various references exist in the literature on the relationship of microstructure and combustion characteristics of gun propellants with microporosity. In particular Weapons Systems Research Laboratory (WSRL) of Salisbury, South Australia is currently engaged in research on porous propellants, in which non-interconnected approximately spherical pores or cavities of 5-20  $\mu$  diameter are randomly dispersed in a single-base propellant matrix. This porosity is induced by incorporation of potassium nitrate in the propellant matrix prior to extrusion and subsequent salt removal by leaching during water steeping operations. These porous propellants have been explored in both closed bomb and strand burners, where it has been shown that small amounts of porosity lead to disproportionate increases in burning rates (Ref. 6 thru 9). It has been the objective of the WSRL group to quantify the relationship between porosity and burning rate, with the benefit of the insight gained from detailed knowledge of the microstructure of these porous propellants.

A comparison of WSRL strand burning rates for a non-porous propellant and for a porous propellant with 10% porosity and 10  $\mu$  pore size is shown in Figure 29 to illustrate the similarities in observed strand burn rate behavior with Hercules, ABL PVN/nitramine propellants. Significant "outliers" in the WSRL burning rate data for the porous propellant are observed, giving occasional apparent burning rates 4-10 times higher than the non-porous propellant in the pressure regime 1,000 - 20,000 psi. For strand burner pressures exceeding 20,000 psi there is an apparent convergence of the porous and non-porous burn rate data.

The question is raised at this point, what is the mechanism responsible for the high apparent burn rates observed for solid propellants containing internal voids or cracks? The phenomenon of rapid flame propagation into the propellant pores or internal microcavities or cracks together with the subsequent rapid regression of the burning surface is termed convective or penetrative burning. The convective burning rate of porous propellant strands often exceeds the nominal (conductive) linear burning rate. In the early 1960's Taylor (Ref. 10) conducted experimental tests to evaluate the convective burning of porous propellants. He observed a critical pressure above which hot gas can penetrate into the porous propellant and significantly increase the regression rate of the charge. The Russian work of the sixties and seventies also cites the transition from conductive to convective burning in porous propellants and the existence of a critical pressure for the transition (Ref. 11 thru 14). The paper of Belyaev, Ref. 11, states that flamespreading into the interior of the porous material leads to an increase in pore pressure and this internal pressure almost completely determines the subsequent development of the process irrespective of the external pressure. The investigation of convective burning in solid propellant cracks has also been studied by Kuo



and associates at Pennsylvania State University (Ref. 15 thru 18).

The anomalous pressure excursion waveforms observed in selected strand burner tests of Control Lot ISB 7797 may be attributed to the transition to a convective or penetrative burning process in the internal microcrack, i.e., connected porosity, structure. The pressure excursion waveforms observed in Lot ISB 7797 strand burner tests suggest a critical pressure for the onset of this convective burning phenomena. Figure 30 shows a plot of "transition" pressure versus applied hydraulic pressure. No correlation is evident except for the fact that the discontinuous behavior in pressure generation is not observed for pressures exceeding 20,000 psi. This may be a reflection of the fact that at high hydrostatic pressure loadings the radial compression of the porous propellant grain reduces the microcrack gap width below some critical value required for gas penetration. This may also be the explanation for the apparent convergence of the strand burn rate data for porous and nonporous propellants observed by WSRL in Figure 29.

It should be recalled that the PCRL high pressure hydraulic strand burner does not operate as a true constant pressure bomb but operates on the principle of small pressure production by the limited gas evolution from the burning process of a small 0.5g propellant strand. The approximate 500 psig pressure rise recorded in the PCRL strand burner provides the driving pressure to initiate the penetrative burning mechanism with the microcracks of the porous propellant grain. It was speculated that the magnitude of the penetrative burning effect would be greatly enhanced in a high pressure closed bomb experiment since the mechanism driving the phenomenon is enhanced by the rapid, large magnitude self-pressurization of the closed bomb associated with the propellant burning process itself. This will be seen to be the case in the following section comparing closed bomb and strand burn rate data.

## 6.0 Comparison with Closed Bomb Burn Rate Data

On Contract DAAK10-85-C-0047, PCRL evaluated the burning rate of certain PVN/nitramine formulations from pressure-time records obtained in Hercules, ABL closed bomb firings. A detailed discussion of the closed bomb reduction may be found in Reference 19. Figures 31 through 37 show a comparison of closed bomb burn rate data with strand burn rate data for selected PVN/nitramine lots.

In all cases closed bomb burn rate data are higher than corresponding strand burn rate data, except for Lot ISB 7799, Figure 31. In this particular case we believe that the closed bomb firings were conducted with a fraction of the lot that was cured differently from the fraction utilized in PCRL high pressure strand burner firings. Also, in those cases where strand burn rate data show unacceptably high scatter, closed bomb burn rate data show unusually high pressure exponents, i.e., slopes.

The question arises, why do closed bomb burn rate data deviate so dramatically from strand burn rate data, and why are the apparent closed bomb burn rates so high?

In the closed bomb environment rapid, large magnitude self-pressurization of the chamber is associated with the propellant burning process itself. Combustor pressurization rates are typically of order 10 Mpsi/sec in the Hercules, ABL 90 cc Impulse Bomb. This high chamber pressurization rate is exacerbated by the augmented penetrative or convective burning process within the porous propellant granules, in which an increase in the rate of convective heat transfer within the micropore cavities significantly enhances the rate of internal flamespreading and internal surface gasification. The influence of chamber pressurization rate on the internal pressurization process within solid propellant cracks has been studied by Kuo, Ref. 15. In fact, pressurization rate within the microcrack structure can far exceed the chamber pressurization rate leading to crack propagation (internal stress loading) and a concomitant increase in surface available for burning. Dynamic burning phenomena associated with this rapid pressurization transient further enhances the gas generation rate.

The details of the structure of the microporosity greatly affect the burning rates deduced from closed bomb firings. Therefore, it is best to call these "apparent" burning rates, which are significantly enhanced over surface or linear burning rates that are more representative of strand burner data. A propellant that is susceptible to the effects of high pressurization rate insofar as gas generation rate is concerned must necessarily exhibit large differences in deduced burning rates from a near-constant pressure strand burner and from a closed bomb. The strand burner should provide propellant burning rate information of a more intrinsic nature while the closed bomb should demonstrate more the transient combustion behavior of the

propellant typical of a gun environment but with lower loading density. It is speculated that as the loading density of the porous propellant in the closed bomb is increased, the apparent burning rate deduced from the p-t data would be increased due to the increased pressurization rate and enhanced convective burning phenomenon.

## 7.0 Conclusions and Recommendations

The results of this study suggest potential ballistic performance improvements of the PVN/RDX propellants over state-of-the-art NC-base small caliber gun propellants. However, additional process improvements are needed to demonstrate the full potential for producing a complexed PVN/RDX gun propellant. The highly nitrated German PVN polymer demonstrated only limited capability for complexation of the nitramine. To assess the potential for complexing higher levels of nitramine, it is essential to examine less nitrated PVN. Also, the processing studies at Hercules, ABL indicated that the cure cycle is instrumental insofar as physical integrity of the extruded propellant grains is concerned. Adjustment of the cure cycle will modify residual solvent removal during processing, thereby affecting the degree of microporosity in the grains.

The most promising PVN/nitramine complexed formulation is Lot ISB 7803. No burn rate pressure exponent shifts are observed in the strand burn rate data and the standard deviation of the data at each pressure point is minimal. Complex Lot ISB 7803 offers significant improvements in propellant energy (impetus) and is a potential candidate for the family of low vulnerability (LOVA) propellants. Vulnerability testing including hot fragment conductive ignition tests (HFCIT) and full scale vulnerability tests are recommended. We are also of the opinion that a reduction of the PVN nitration level will result in further improvements of the vulnerability characteristics.

This class of complexed PVN/RDX gun propellants satisfies the performance requirements of the 25mm XM919 APFSDS round. The product of propellant impetus and charge weight estimated to meet the performance goals is 115,000 j. For a nominal single-perf granulation charge loading of 0.91 g/cc, which is low due to porosity effects, in an available cartridge volume of 96cc, the required propellant impetus is 115,000 j/87.4 g, or 1316 j/g. The thermochemical equilibrium calculations for Lot ISB 7803 place its impetus at 1321 j/g, meeting the performance goals, hopefully without loss of desired insensitivity characteristics. This needs to be explored in follow-on efforts.

## 8.0 References

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TABLE 1.

Nominal Composition (Weight Percent)					Actual Composition (Weight Percent)					Solvent			
	PVN	RDX	HMX	DOA	2-NDPA	PVN	RDX	HMX	DOA	2-NDPA	Moisture	Type	%
ISB 7799 <sup>+</sup>	25.0	---	74.0 , 4.56μ	---	1.0	25.60	---	71.6	---	0.64	0.41	ethanol acetone	1.02 0.73
ISB 7800*	25.0	---	74.0 , 4.56μ	---	1.0	26.60	---	71.8	---	0.84	0.11	acetone	0.65
ISB 7801*	24.5	---	72.52, 4.56μ	2.0	0.98	27.02	---	70.9	0.69	0.84	0.04	acetone	0.51
ISB 7776 <sup>+</sup>	25.0	74.0, N/A	---	---	1.0	---	---	not measured	---	---	---	ethyl acetate	N/A
ISB 7797 <sup>+</sup>	25.0	74.0, 10.44μ	---	---	1.0	25.32	67.6	5.6	---	0.74	0.06	acetone	0.68
ISB 7783*	25.0	74.0, N/A	---	---	1.0	---	---	not measured	---	---	---	acetone	N/A
ISB 7802*	25.0	74.0, 5.35μ	---	---	1.0	27.58	65.6	5.2	---	0.84	0.10	acetone	0.68
ISB 7792 <sup>+</sup>	24.5	72.5, 12.3 μ	---	2.0	1.0	26.18	64.3	7.5	0.66	0.54	0.07	acetone	0.75
ISB 7803*	24.5	72.5, 5.35μ	---	2.0	1.0	28.97	64.3	4.7	0.58	0.85	0.06	acetone	0.54

\* "Complex" propellant

+ Control

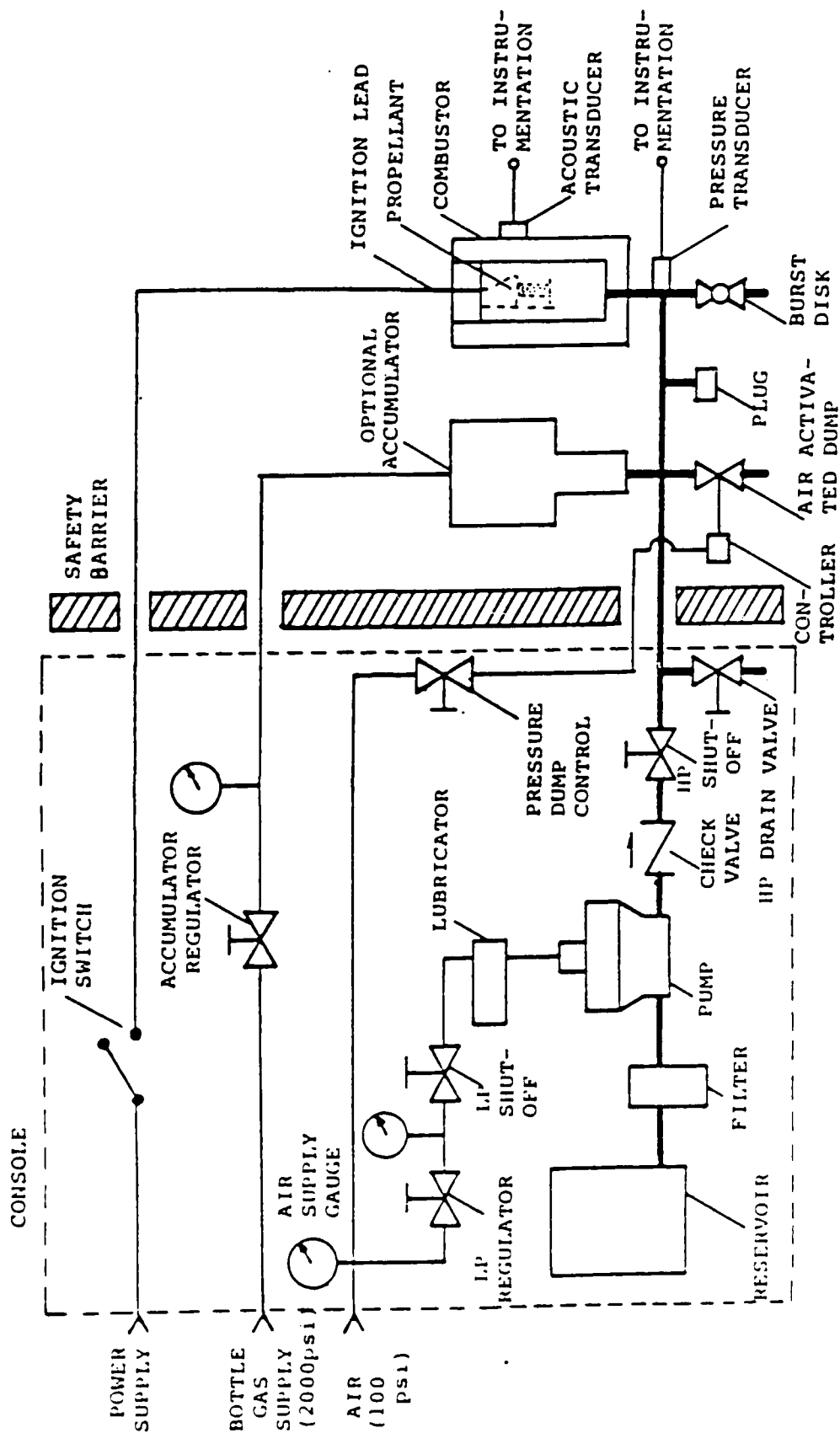
TABLE 2.

EMPIRICAL BURN RATE CONSTANTS

$$r = ap^n$$

		a	n
ISB 7799	PVN/HMX CONTROL	--	--
ISB 7800	PVN/HMX COMPLEX	0.0016982	0.8433
ISB 7801	PVN/HMX/DOA COMPLEX	0.0006149	0.9353
ISB 7776	PVN/RDX CONTROL	(two slope breaks evident)	
ISB 7797	PVN/RDX CONTROL	--	--
ISB 7783	PVN/RDX COMPLEX	0.0003920	0.9878
ISB 7802	PVN/RDX COMPLEX	0.0023676	0.8209
ISB 7792	PVN/RDX/DOA CONTROL	--	--
ISB 7803	PVN/RDX/DOA COMPLEX	0.0005727	0.9334
	JA-2 BASELINE	0.0006304	0.9167

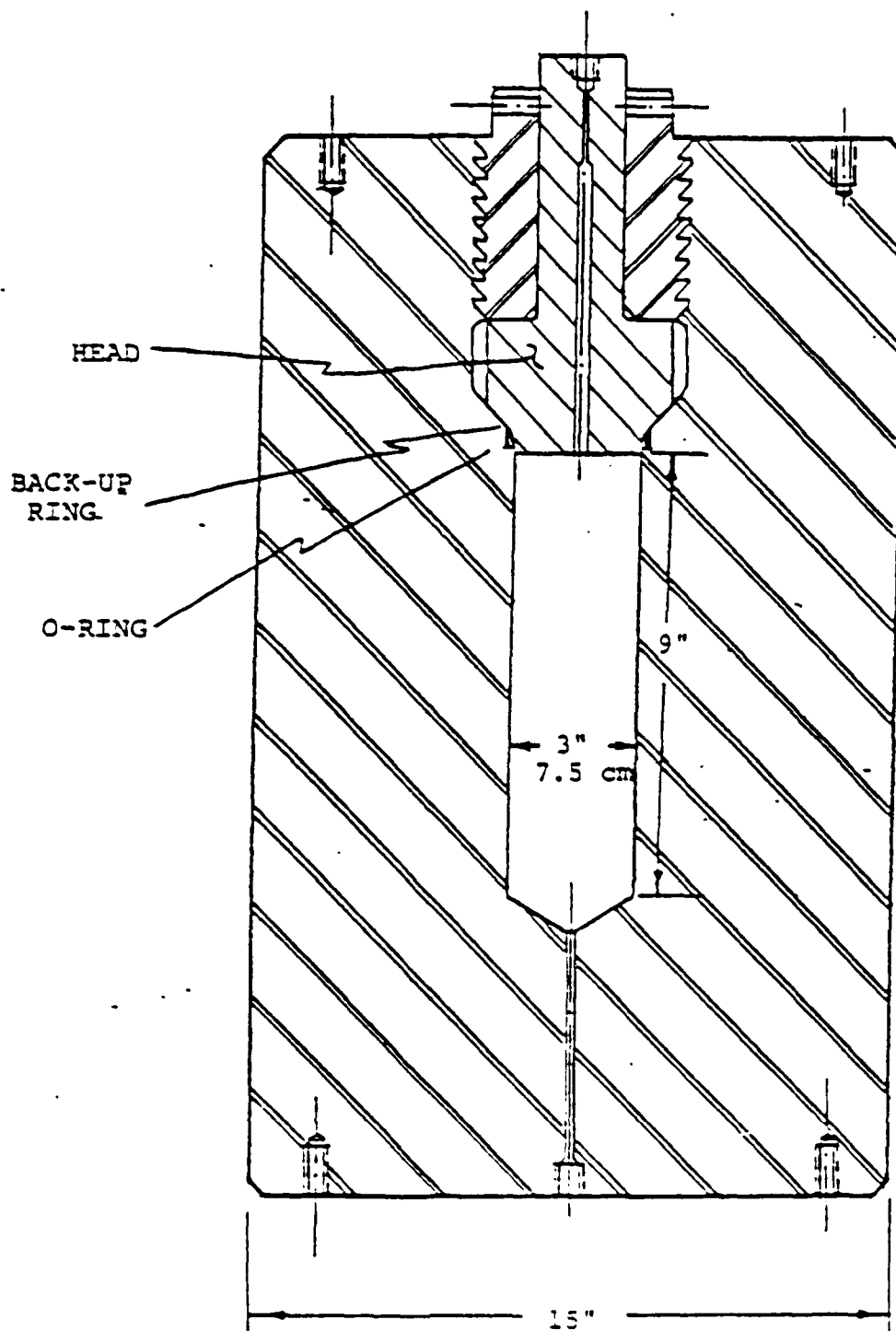




**FIGURE 1.** High pressure combustion system uses a liquid for pressurization. The liquid is pressurized with an air-operated pump.

OPERATING PRESSURE: 50,000 PSI (345 MPa)

DESIGN PRESSURE: 100,000 PSI (690 MPa)



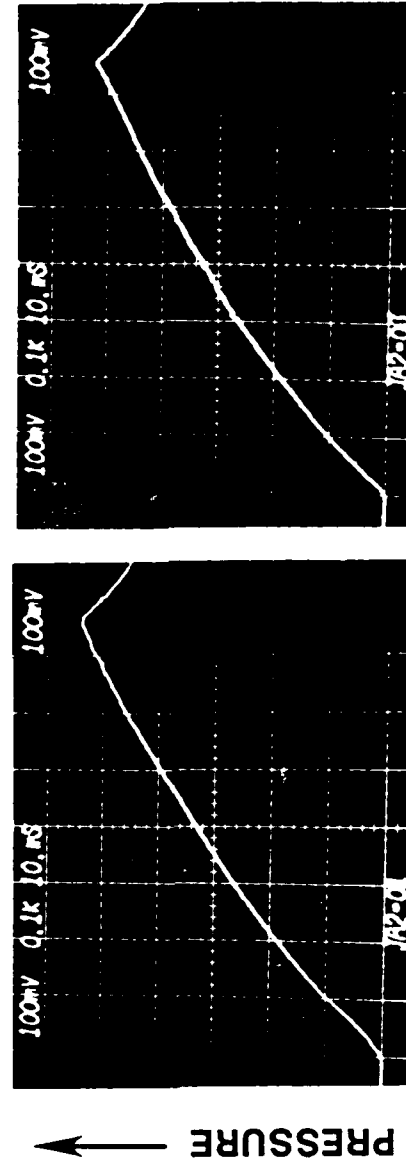
**FIGURE 2.** Configuration of the PCRL High Pressure Strand Burner for Burning Propellant Strands in a Hydraulic Medium, Showing Overall Dimensions.

FIGURE 3.

# PRESSURE EXCURSION TECHNIQUE

HIGH PRESSURE: 40 KPSI

JA-2, LOT HCL85K003-009



TIME SCALE: 10 msec/div

PRESSURE SCALE: 100 psi/div

FIGURE 4.

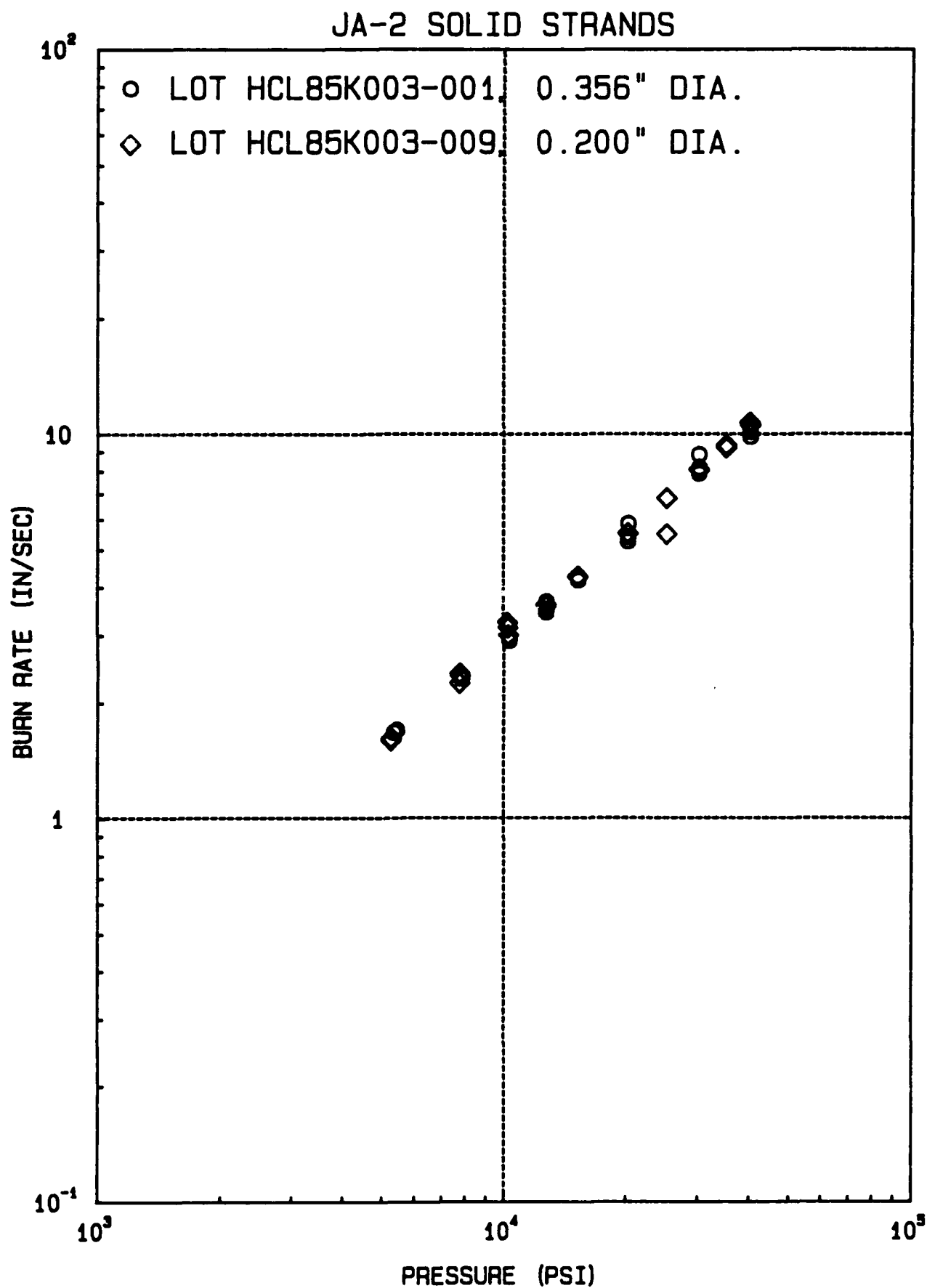


FIGURE 5.

JA-2 SOLID STRANDS

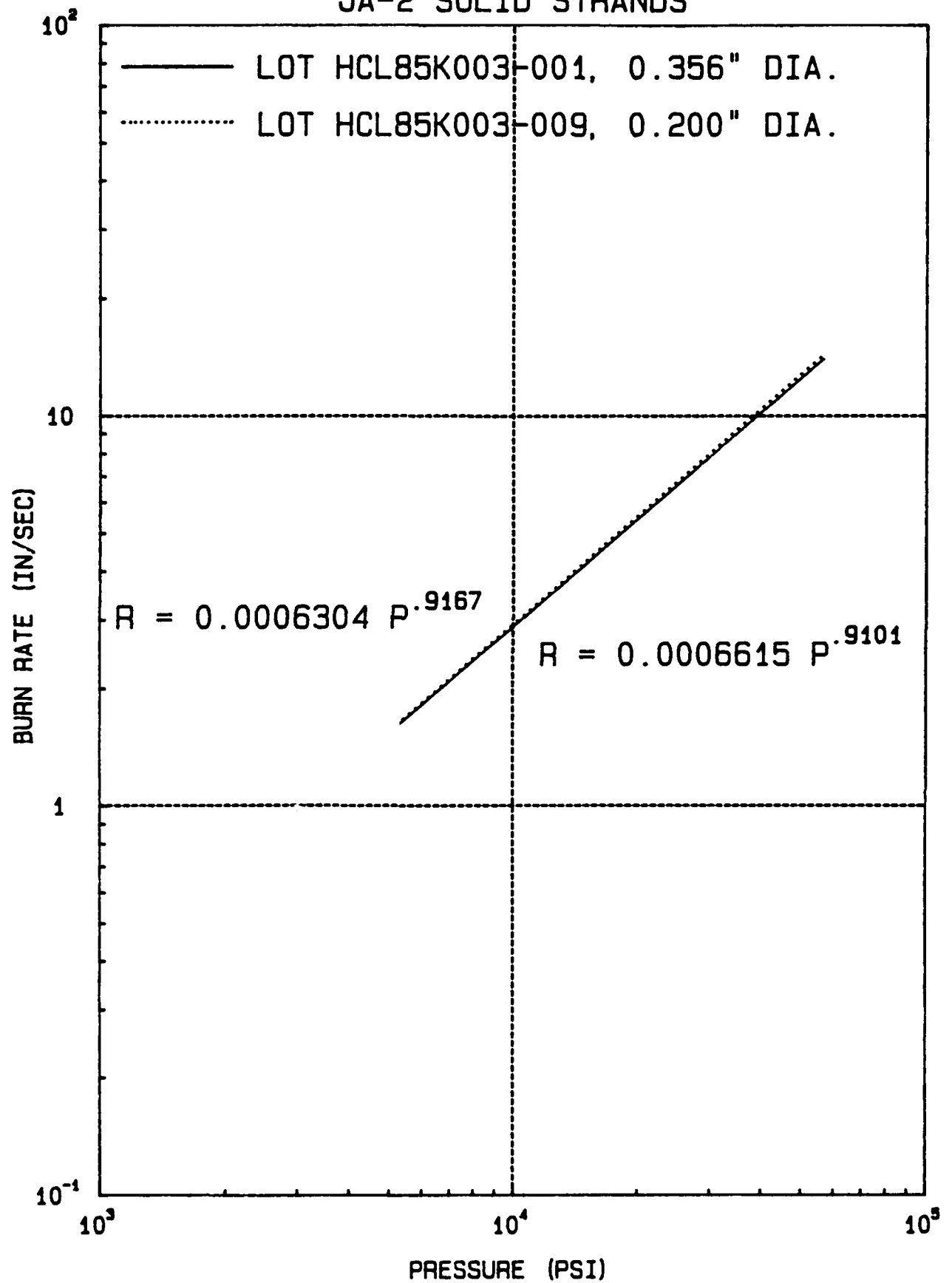


FIGURE 6.

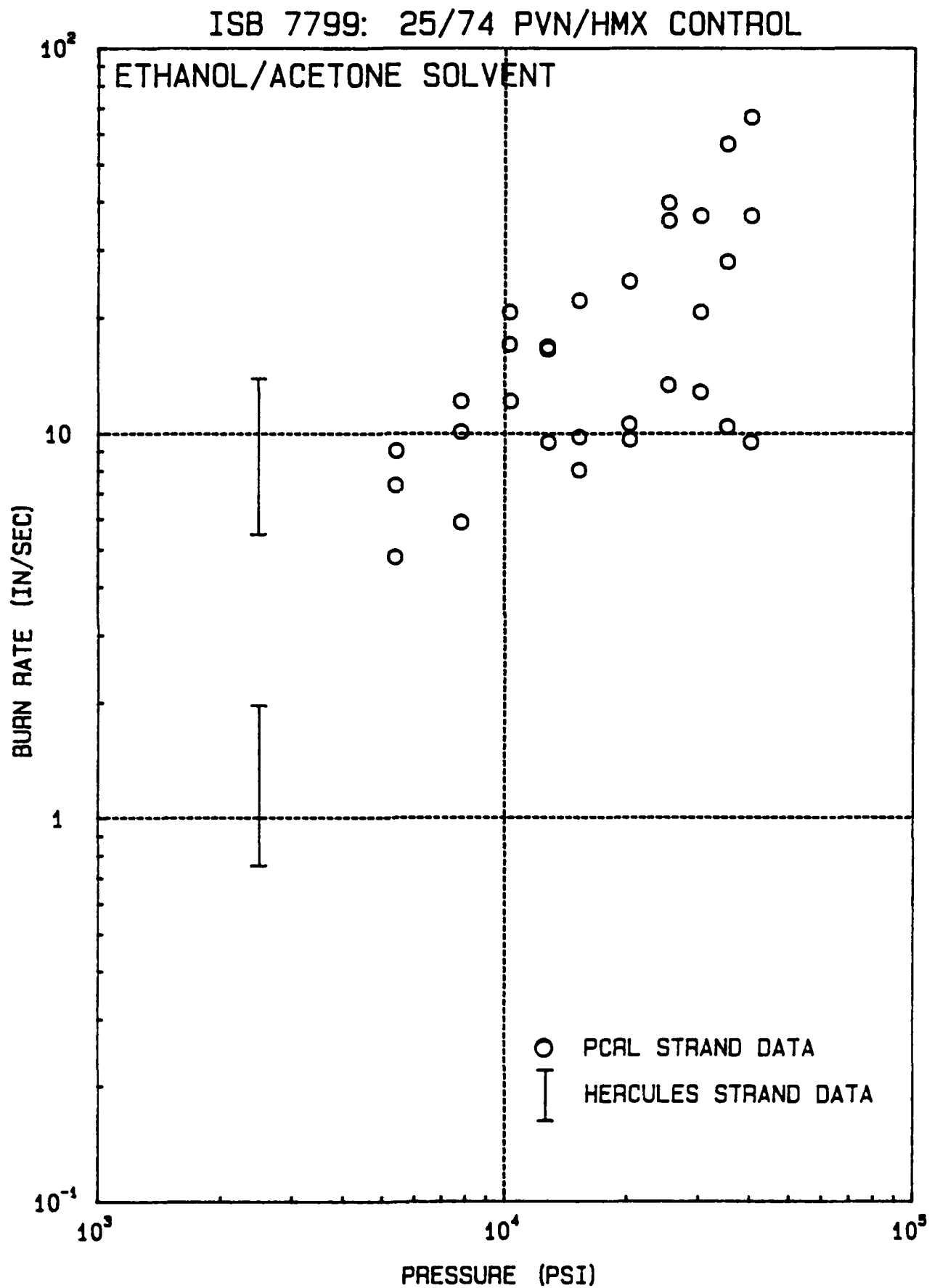


FIGURE 7.

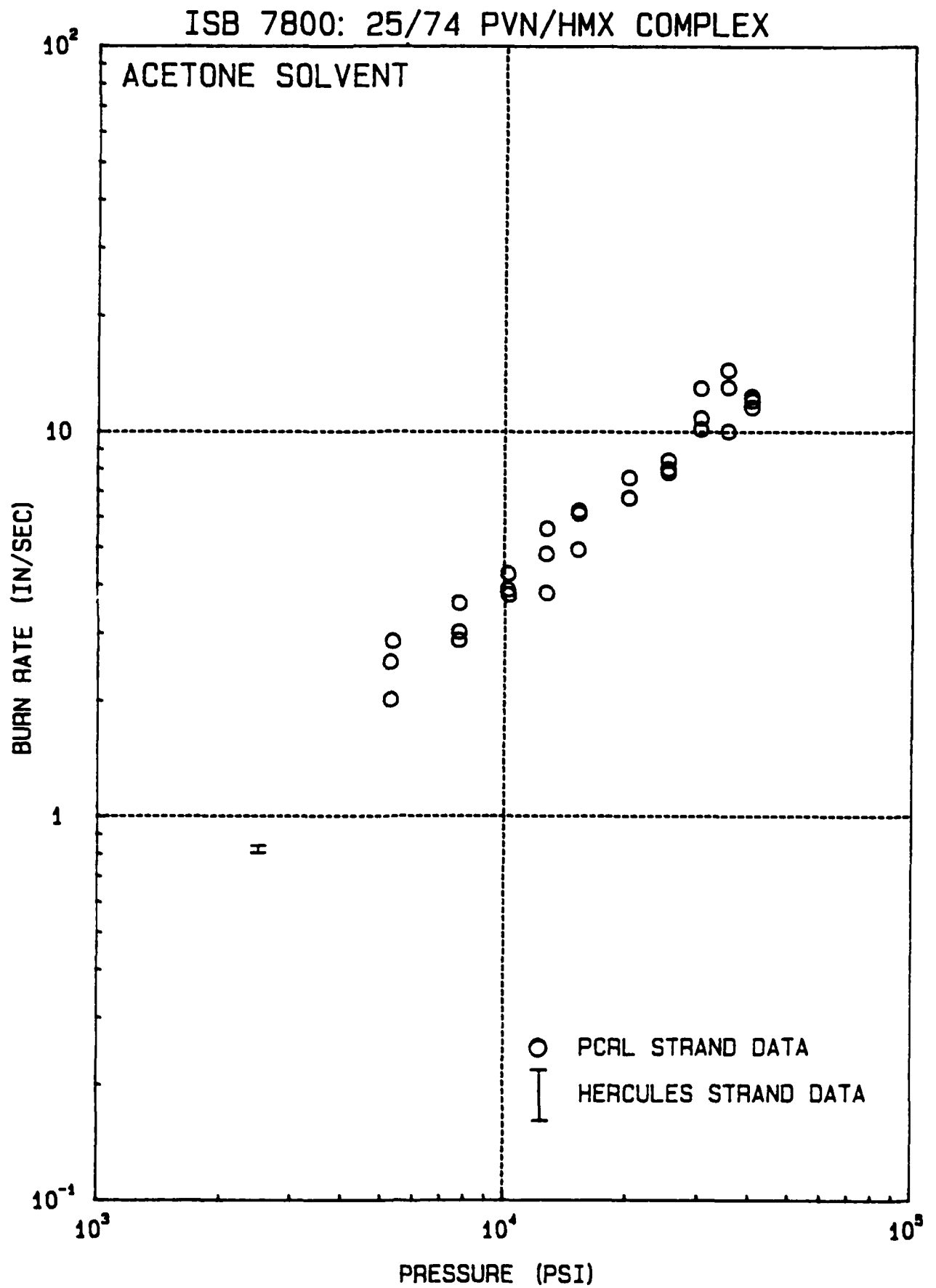


FIGURE 8.

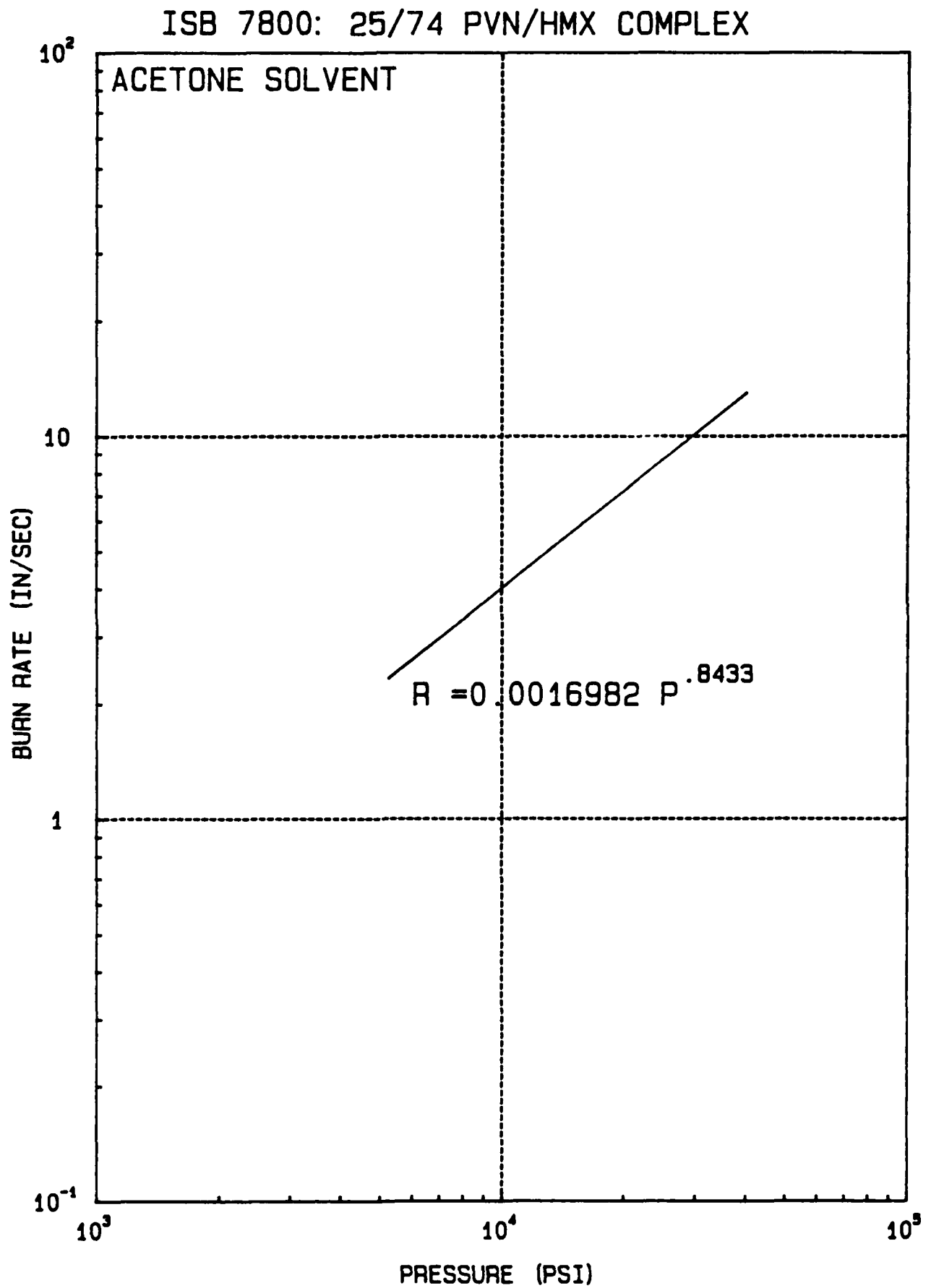




FIGURE 9.

ISB 7801: 24.5/72.5/2.0 PVN/HMX/DOA COMPLEX

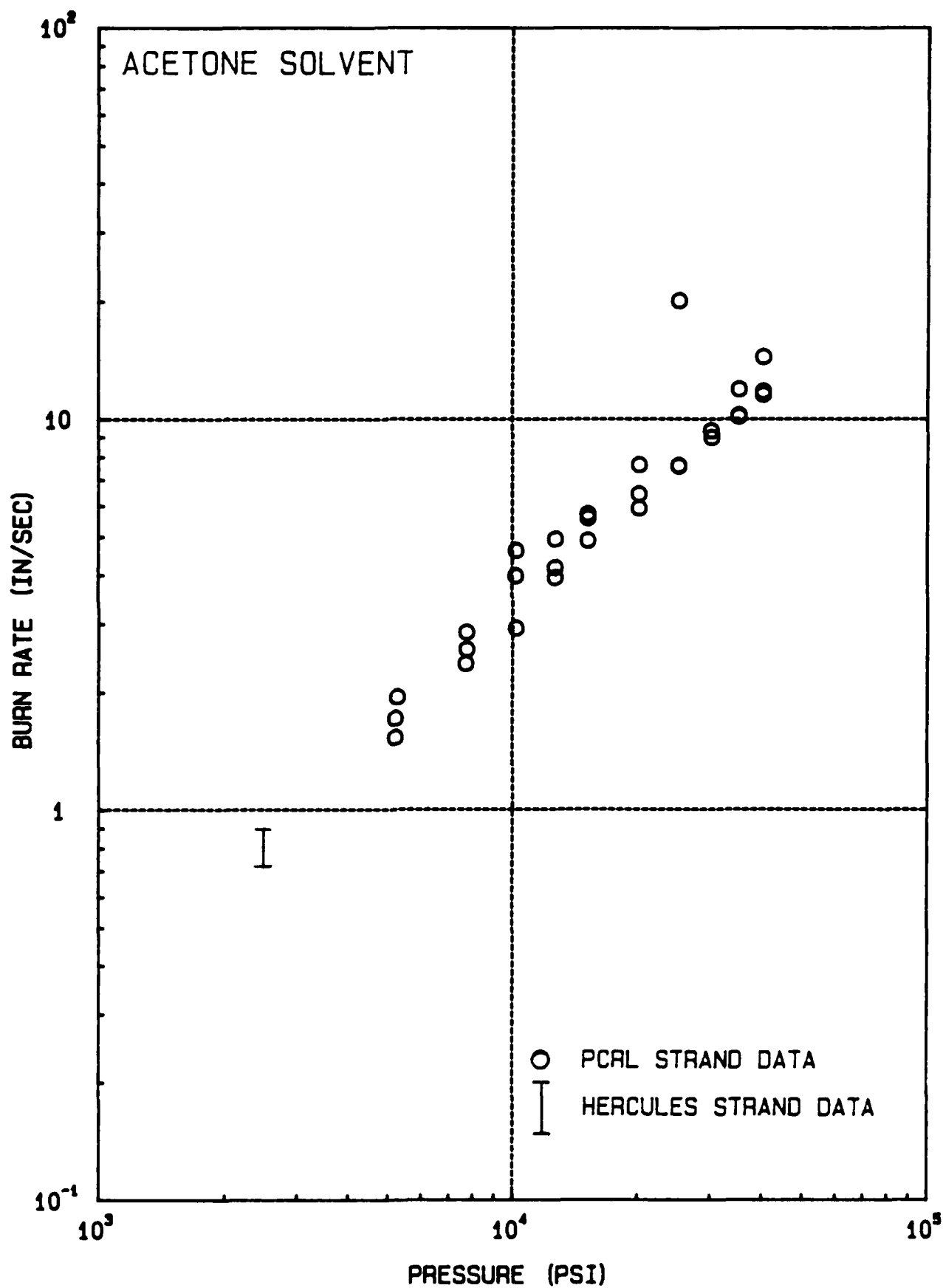


FIGURE 10.

ISB 7801: 24.5/72.5/2.0 PVN/HMX/DOA COMPLEX

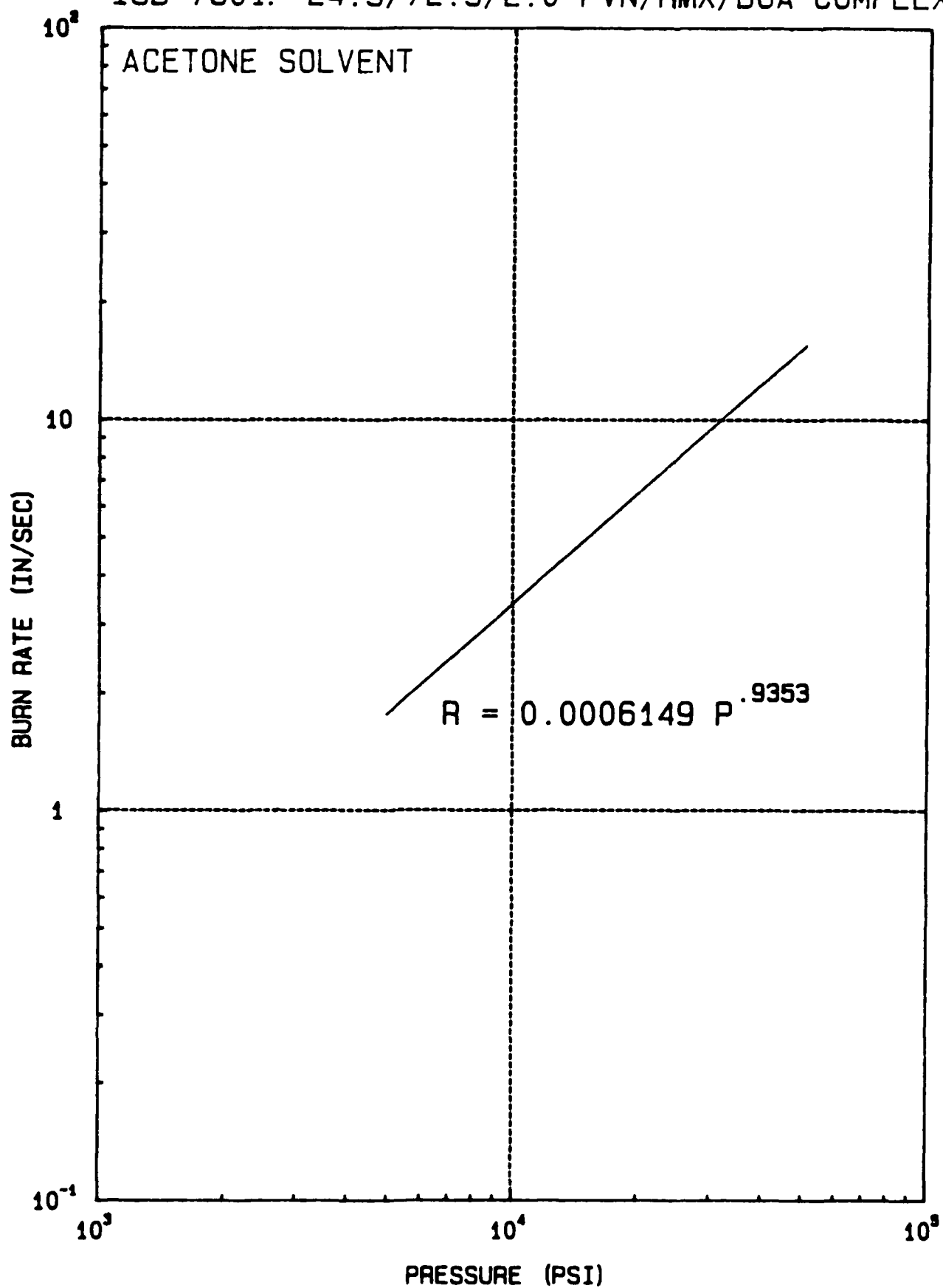


FIGURE 11.

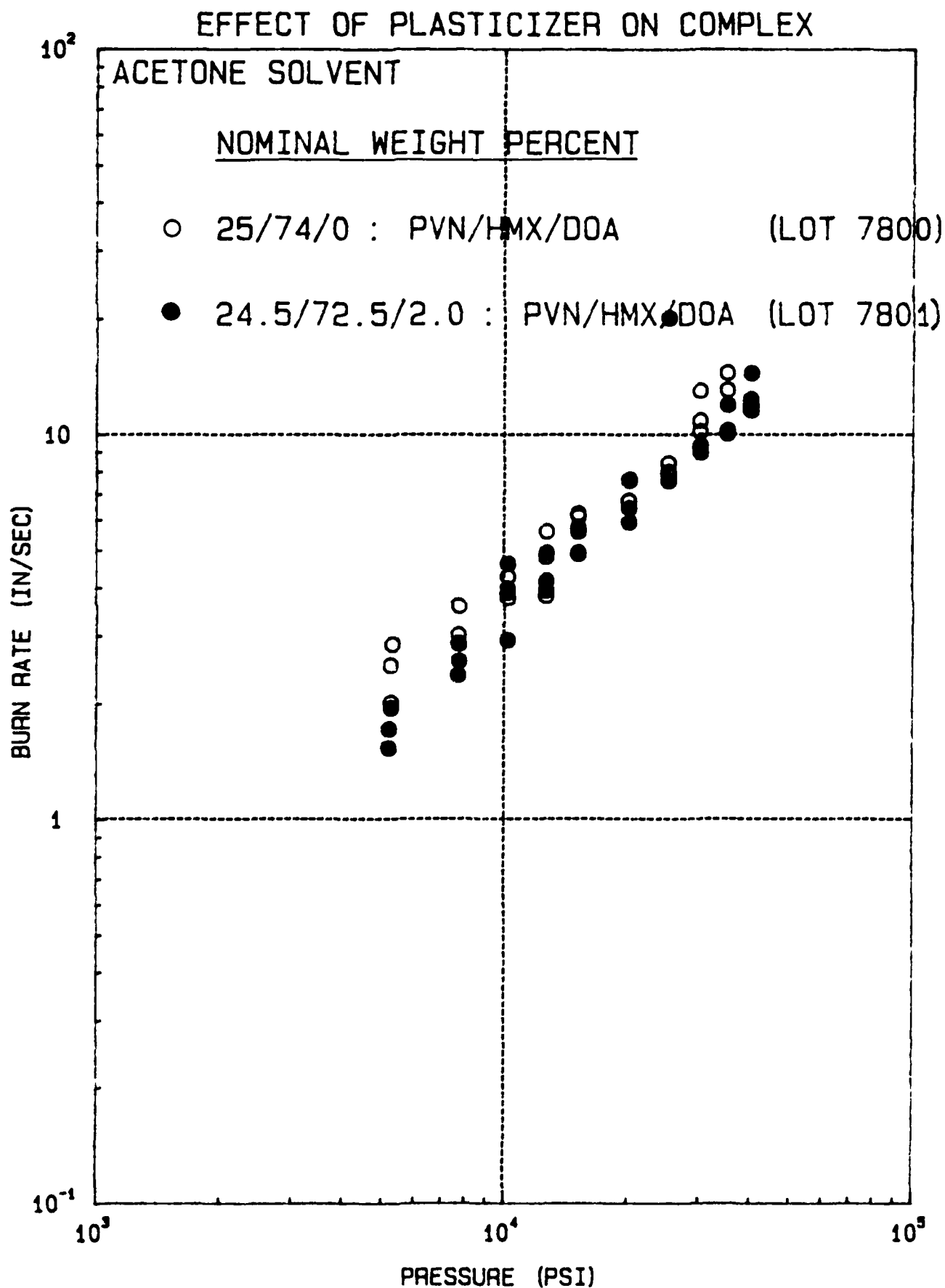


FIGURE 12.

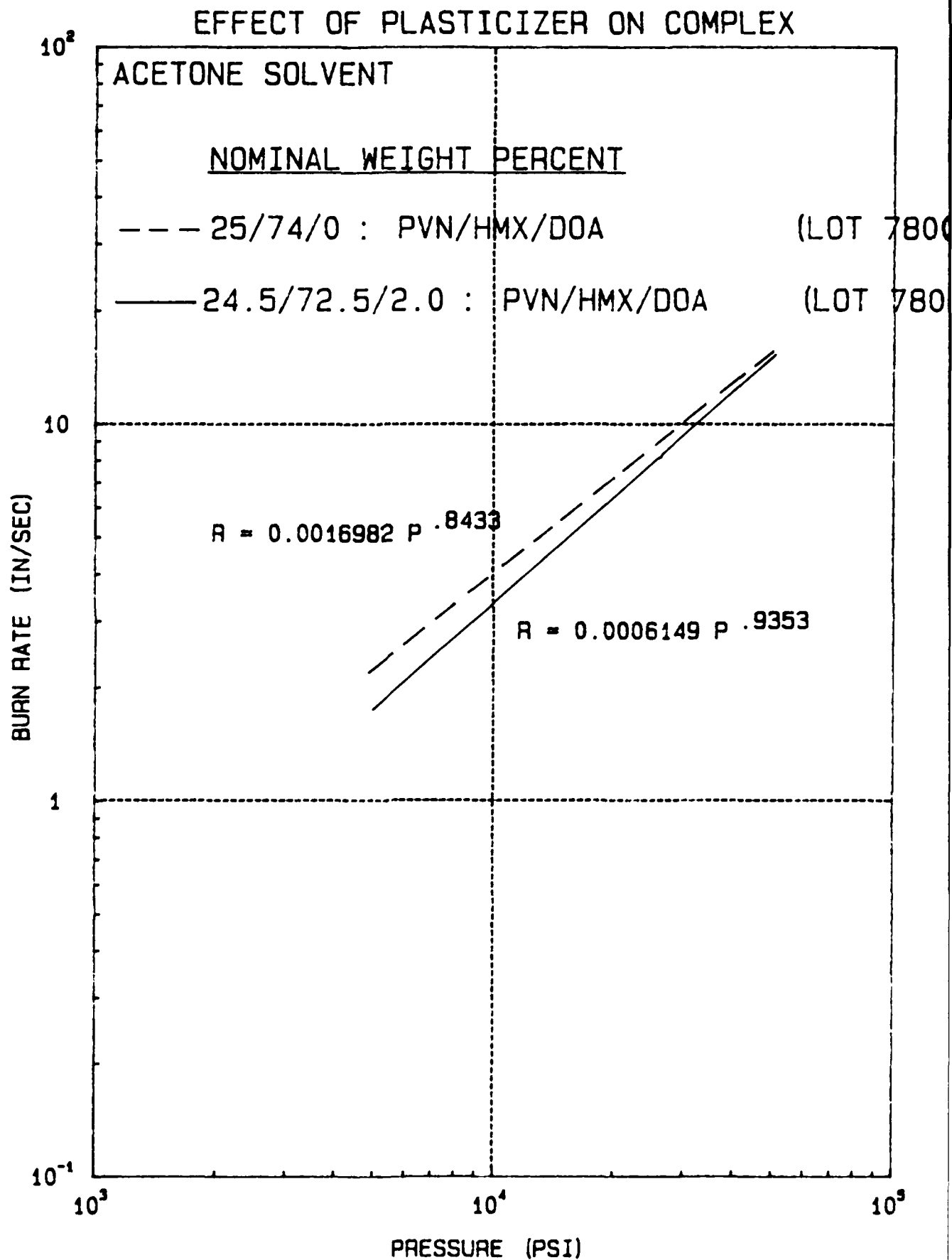


FIGURE 1.3.

ISB 7776: 25/74 PVN/RDX CONTROL

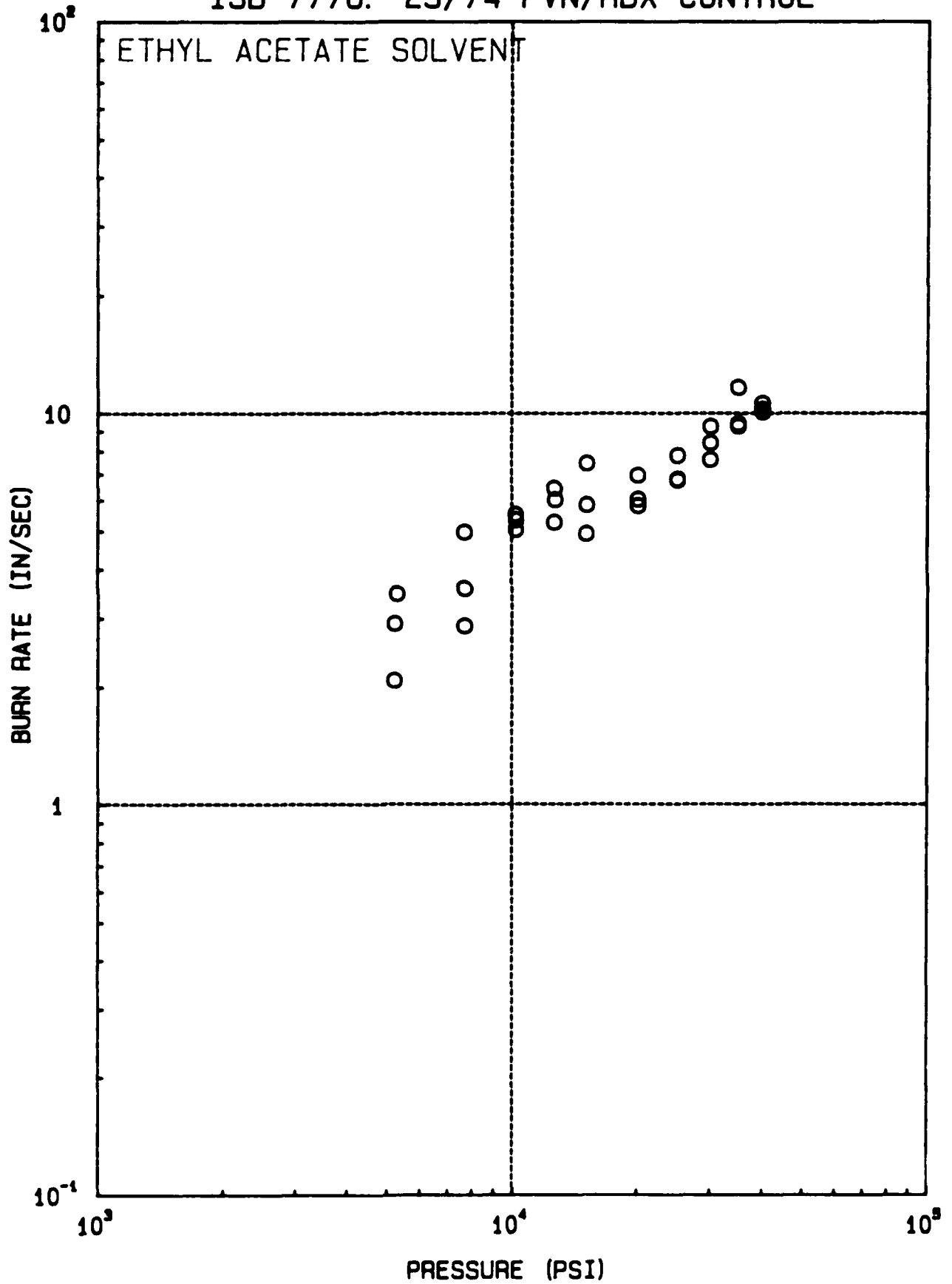


FIGURE 14.

ISB 7776: 25/74 PVN/RDX CONTROL

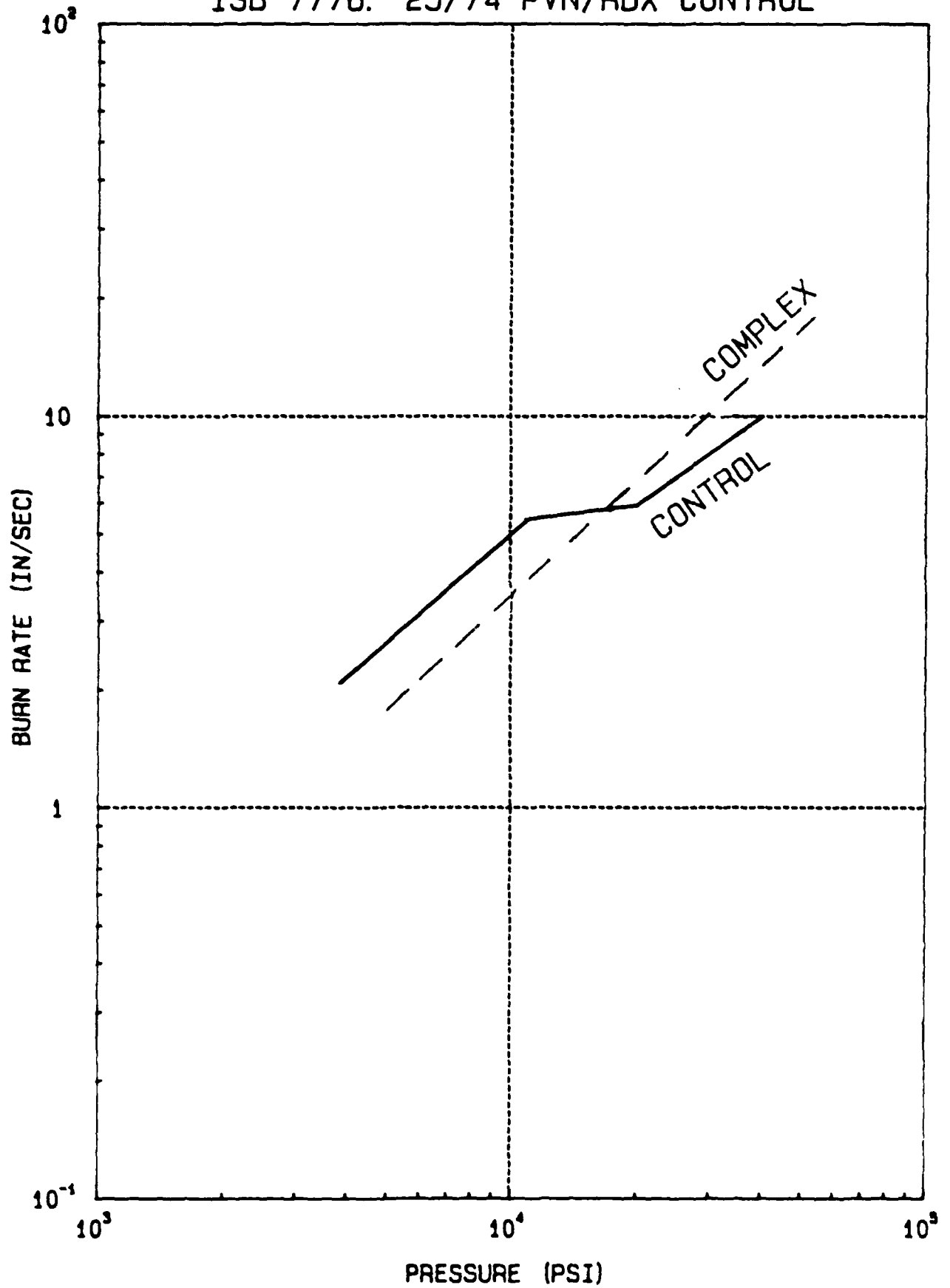


FIGURE 15.

ISB 7797: 25/74 PVN/RDX CONTROL

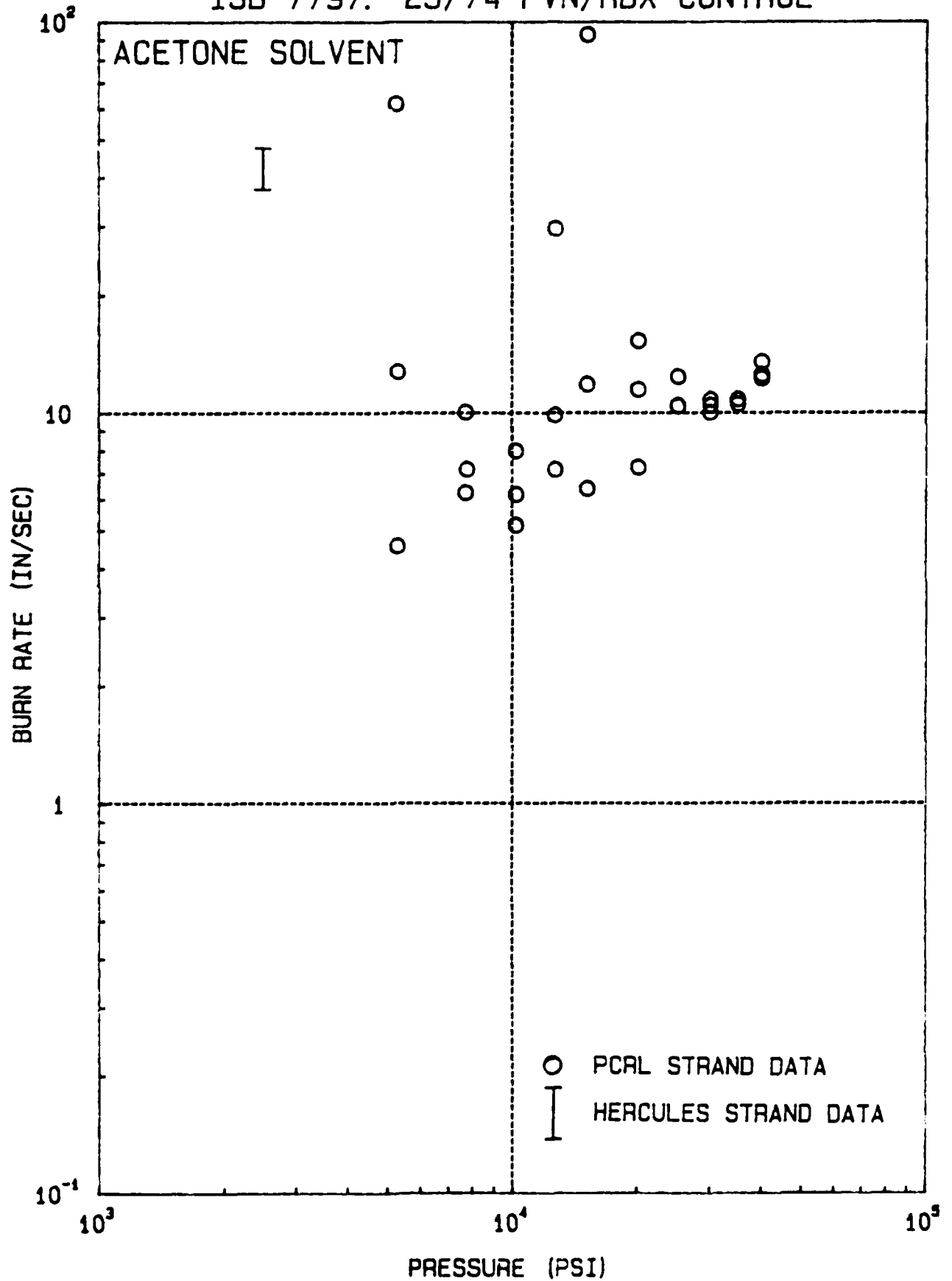


FIGURE 16.

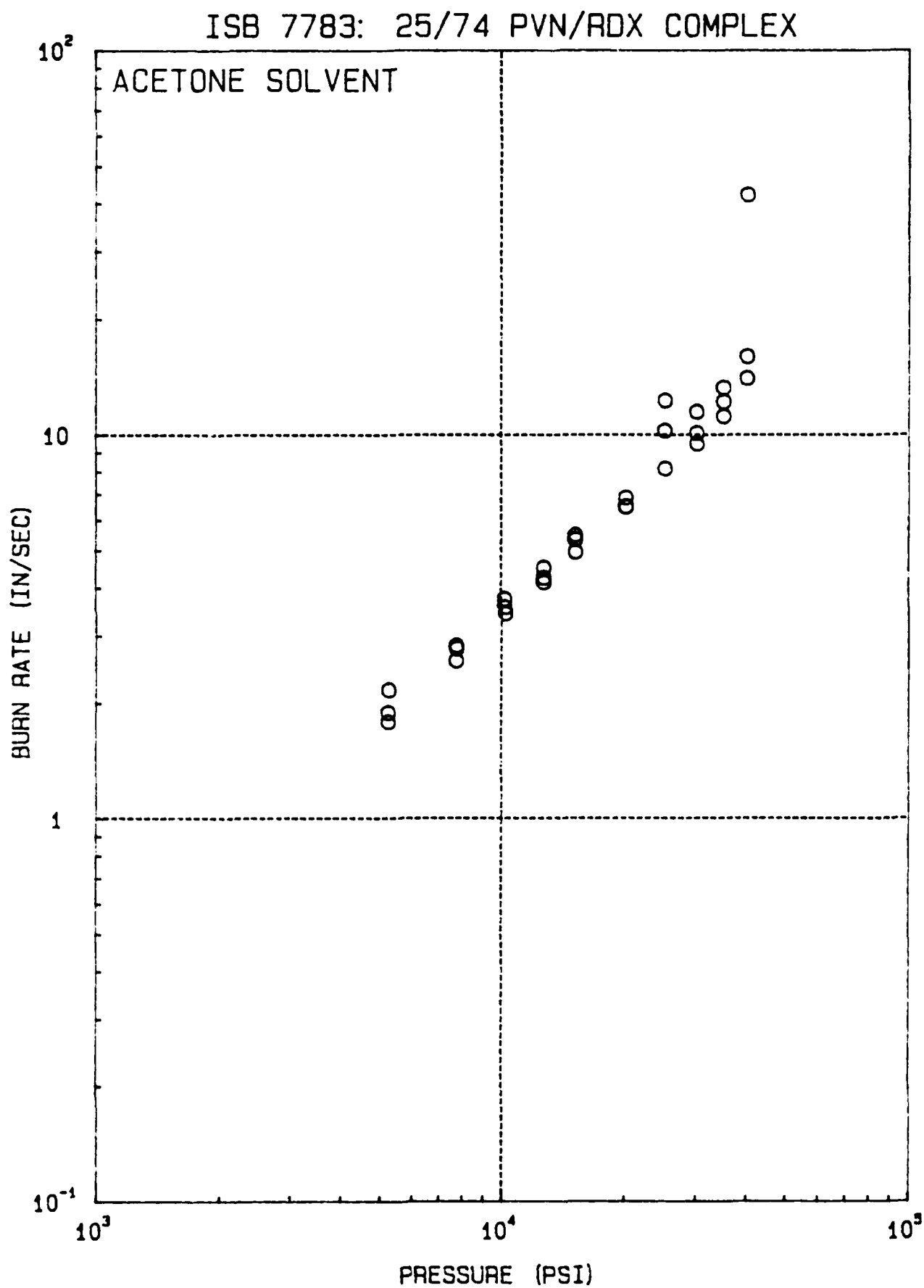




FIGURE 17.

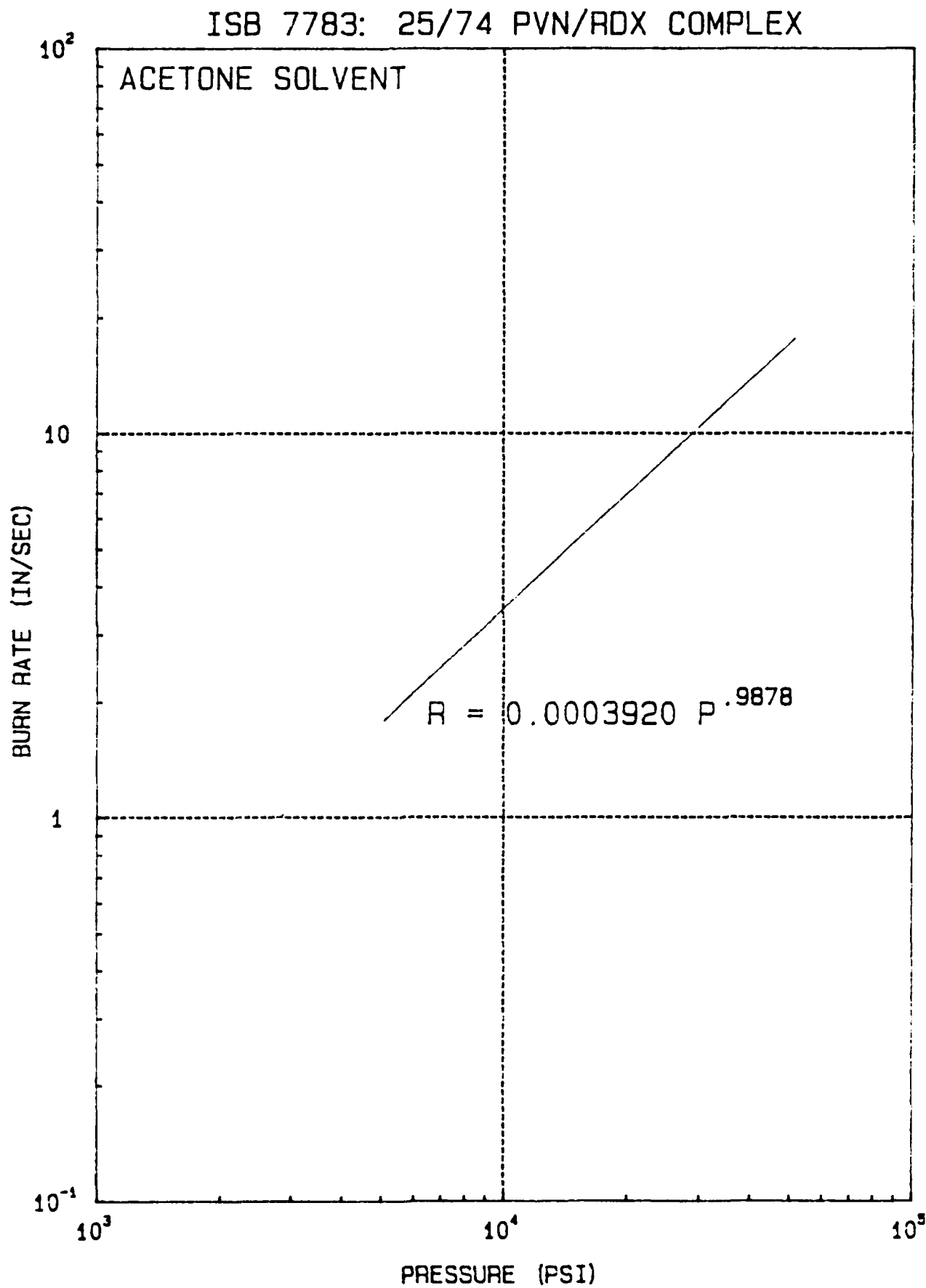


FIGURE 18.

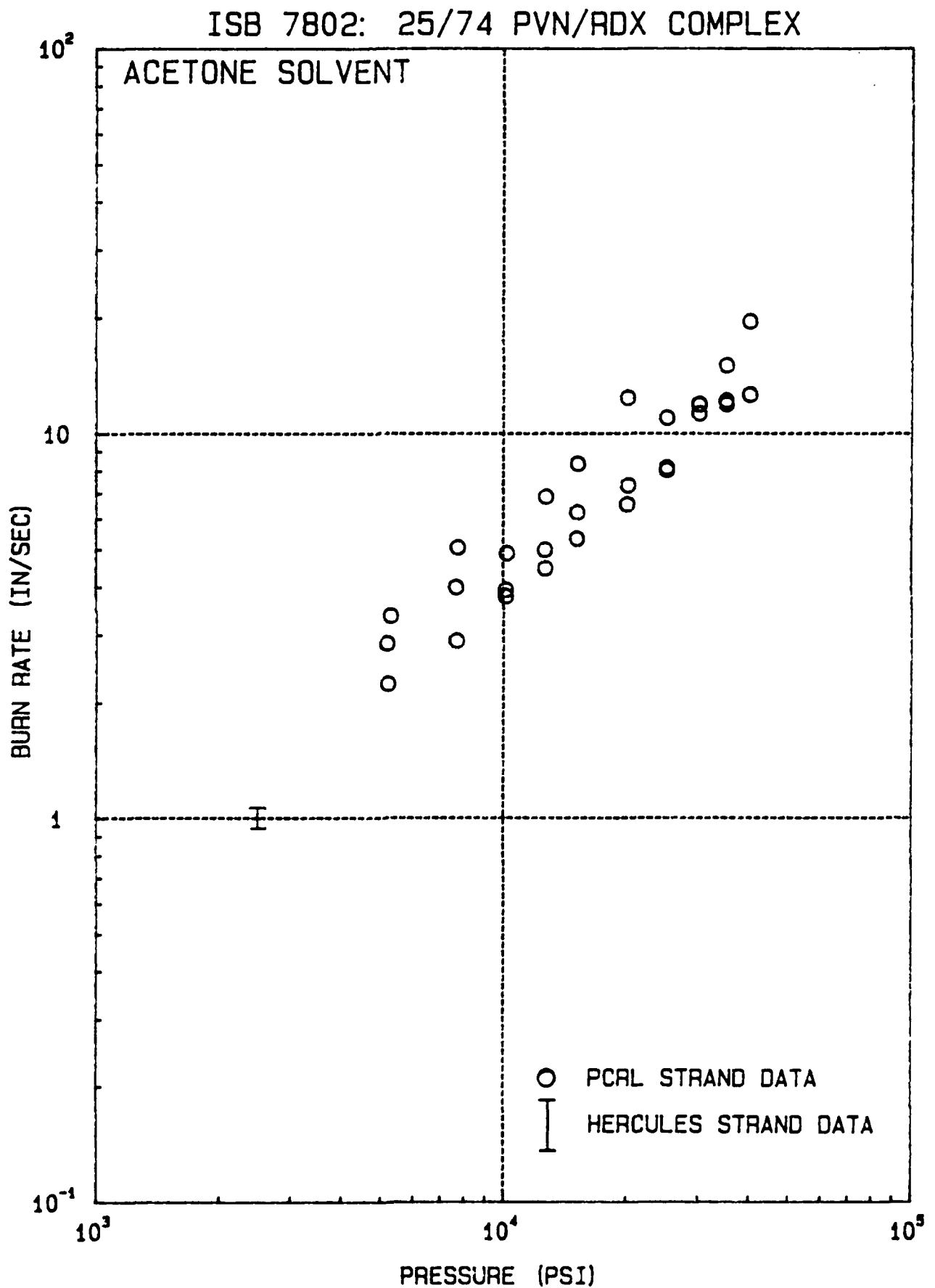


FIGURE 19.

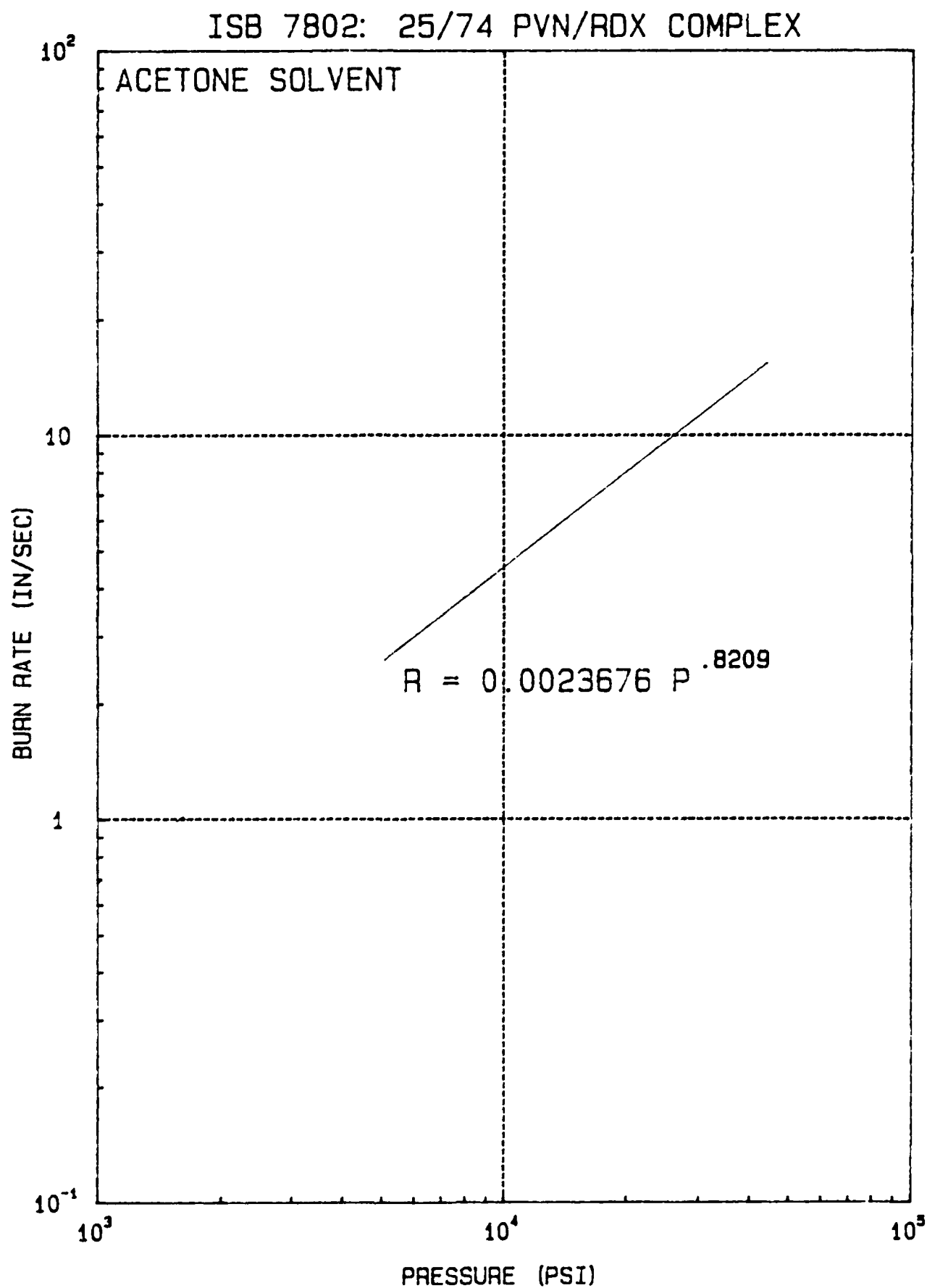


FIGURE 20.

25/74 PVN/RDX COMPLEX

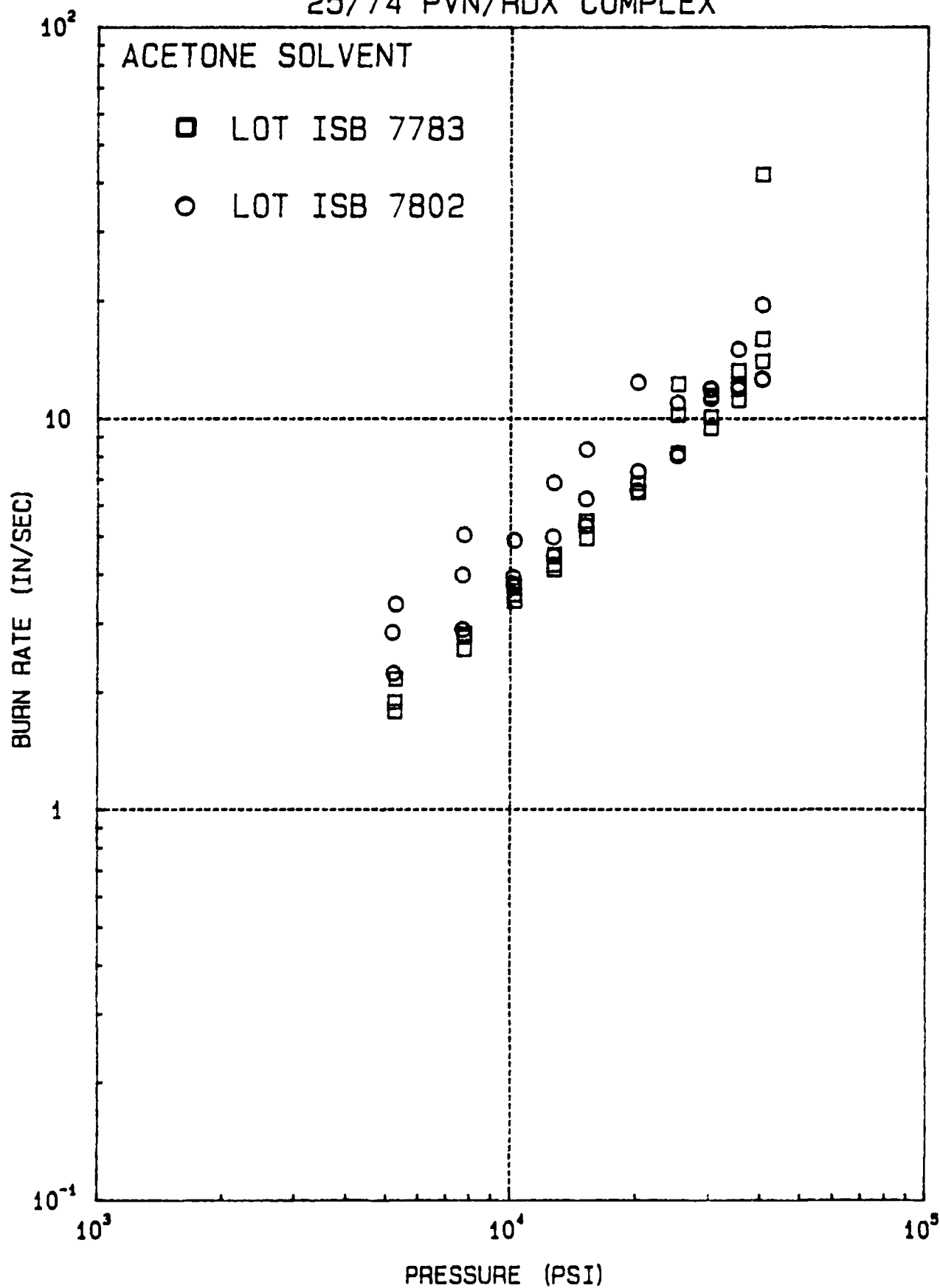


FIGURE 21.

25/74 PVN/RDX COMPLEX

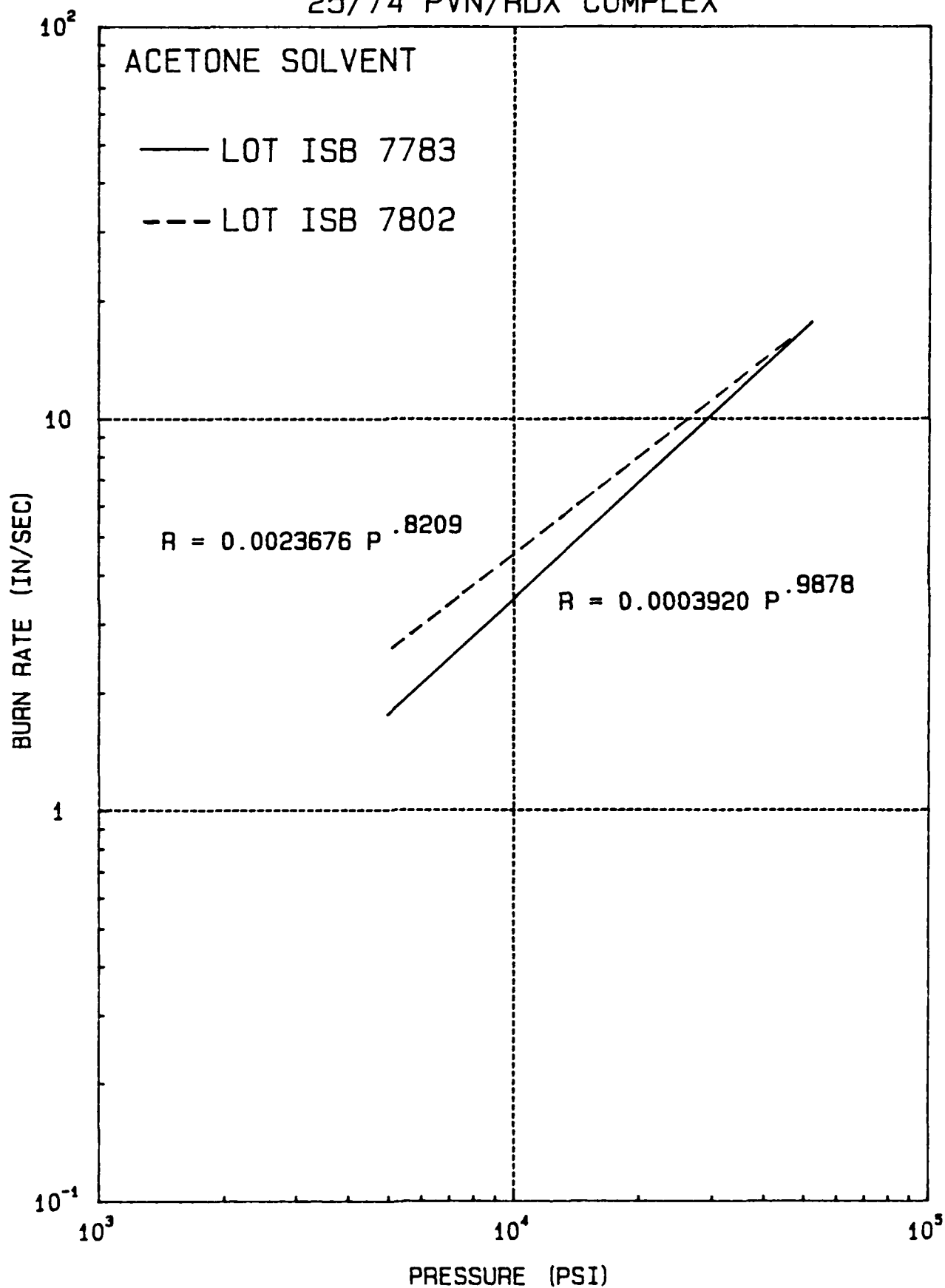


FIGURE 22.

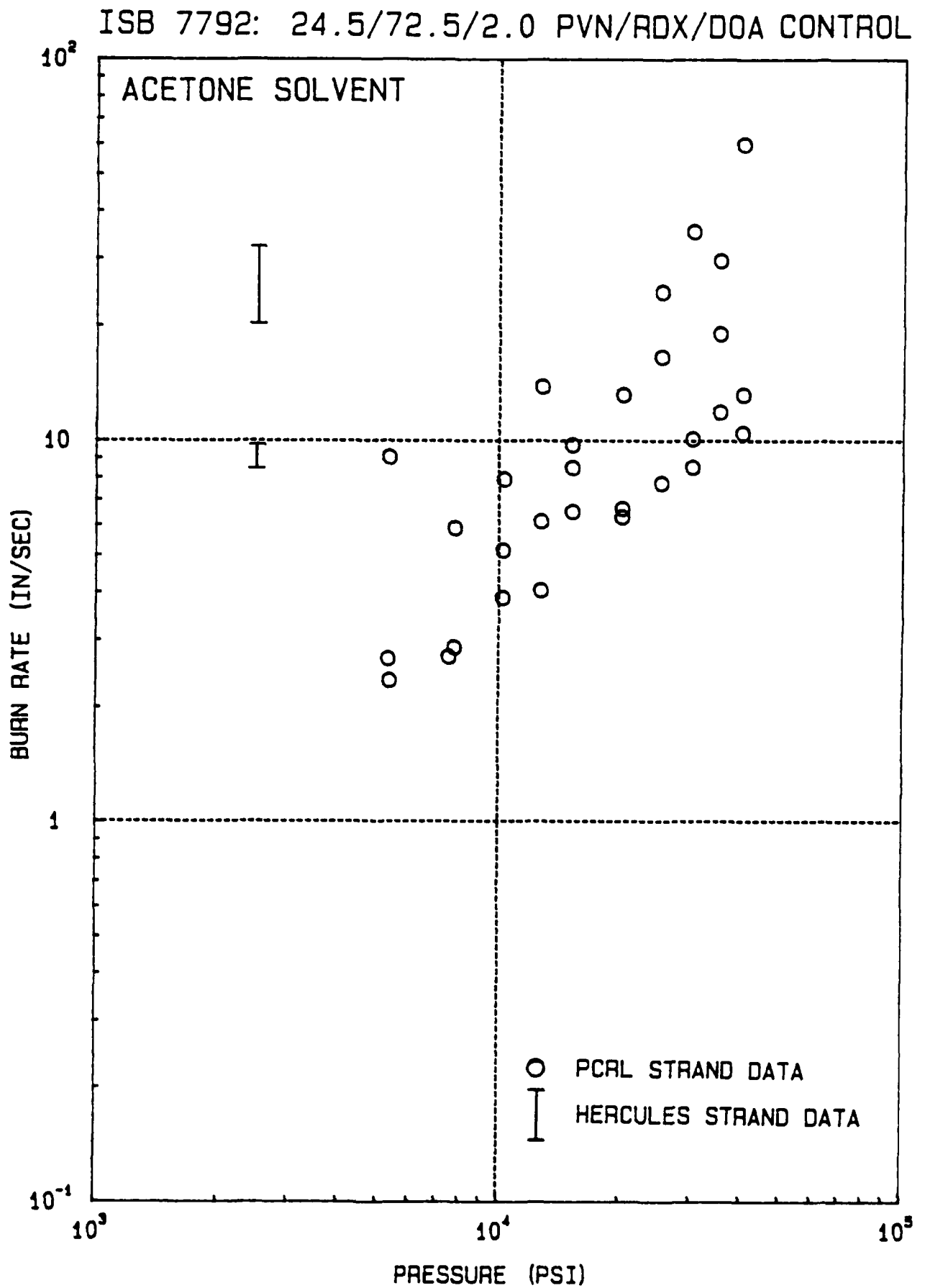


FIGURE 23.

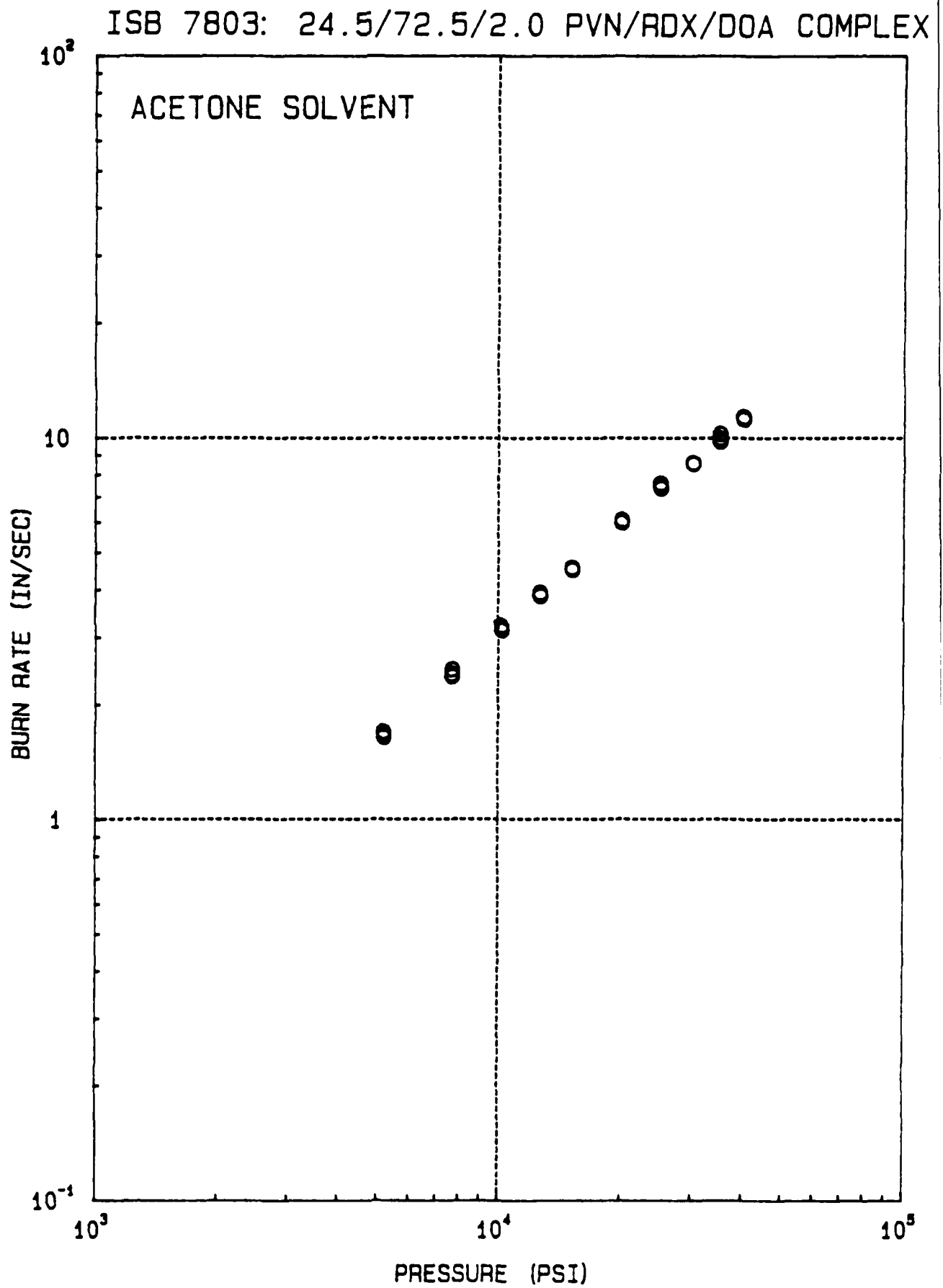


FIGURE 24.

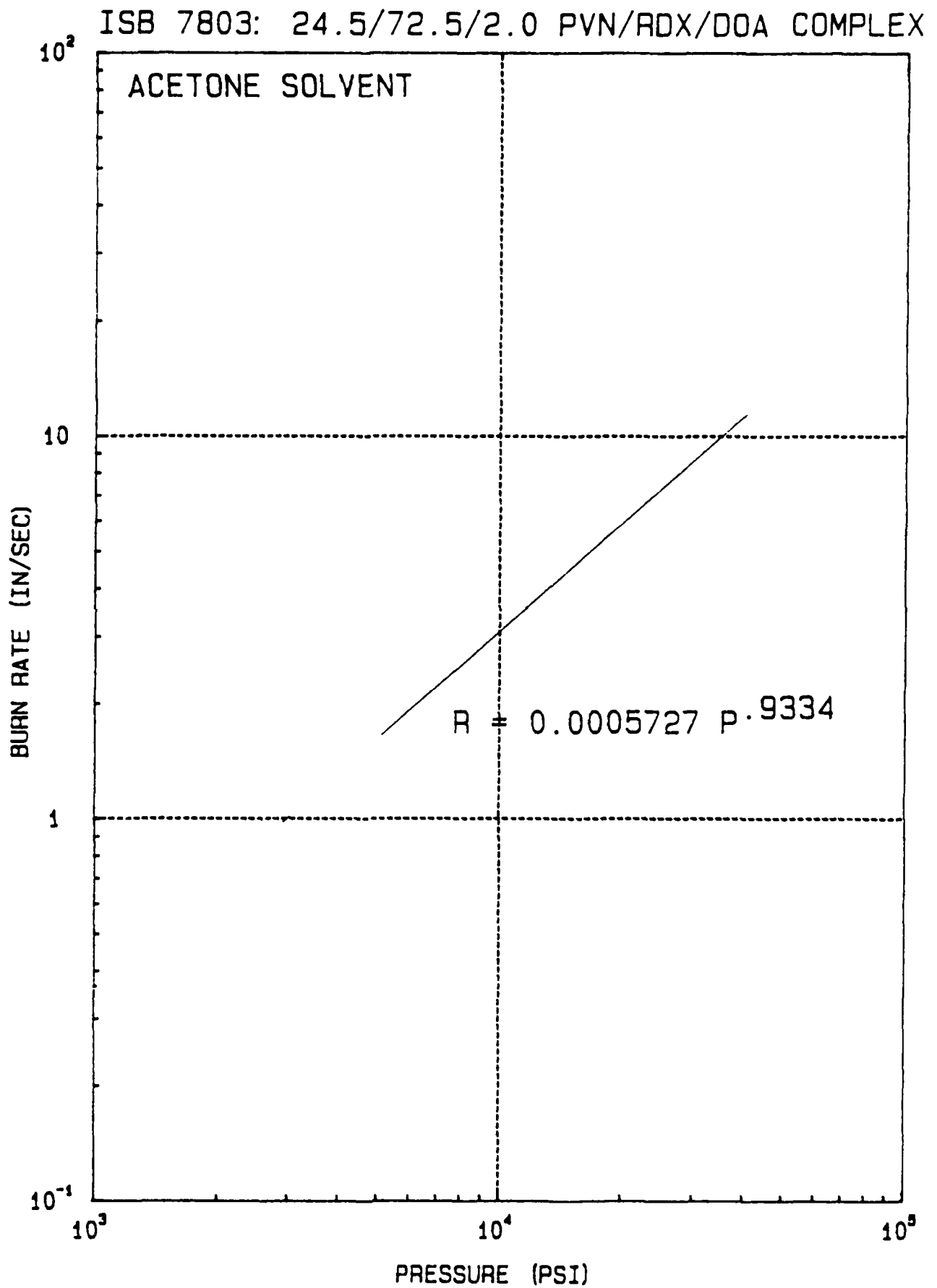




FIGURE 25.

EFFECT OF PLASTICIZER ON COMPLEX

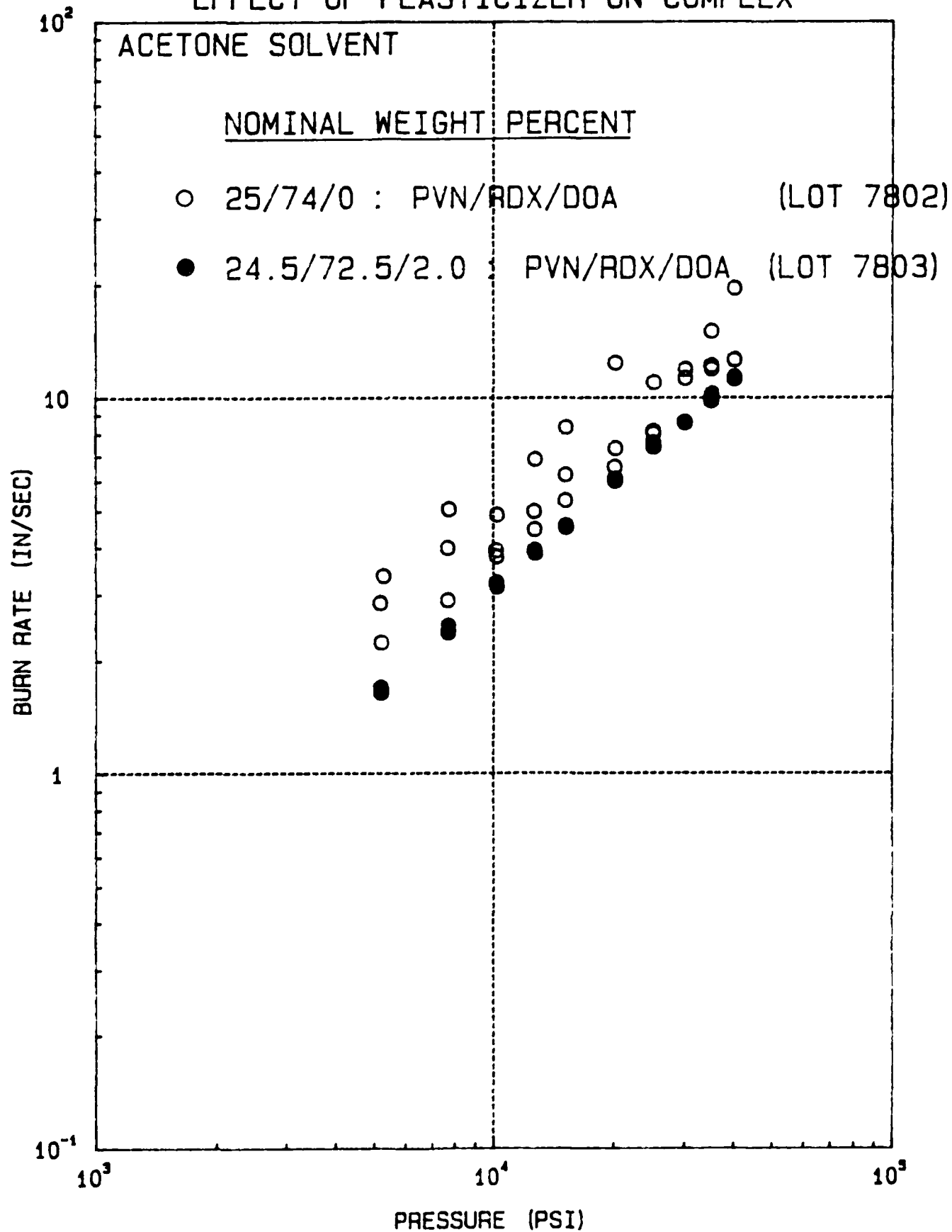
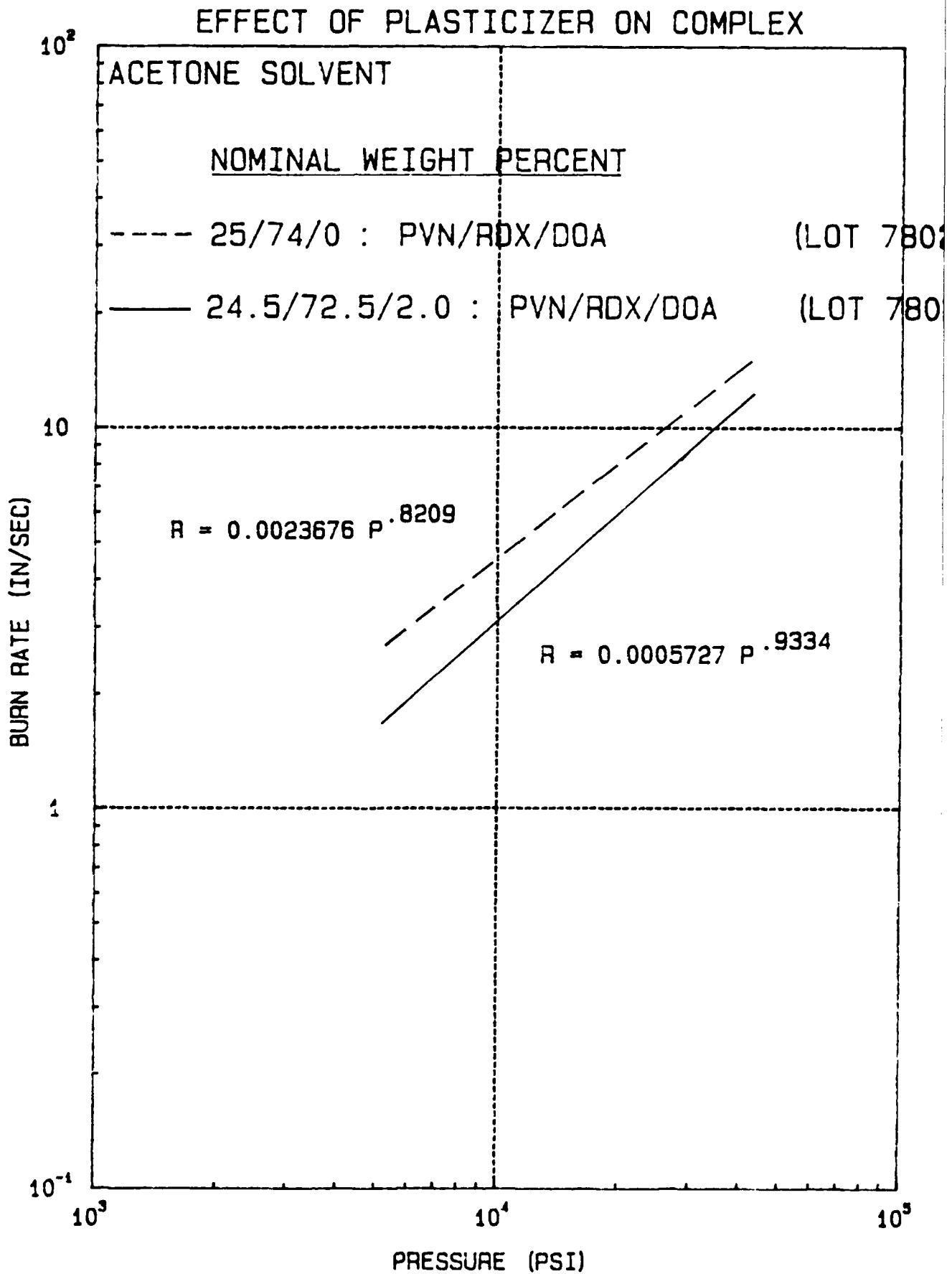


FIGURE 26.



# PRESSURE EXCURSION TECHNIQUE

24.5/72.5/2.0 PVN/RDX/DOA COMPLEX, LOT ISB 7803

PRESSURE SCALE: 100 psi/div

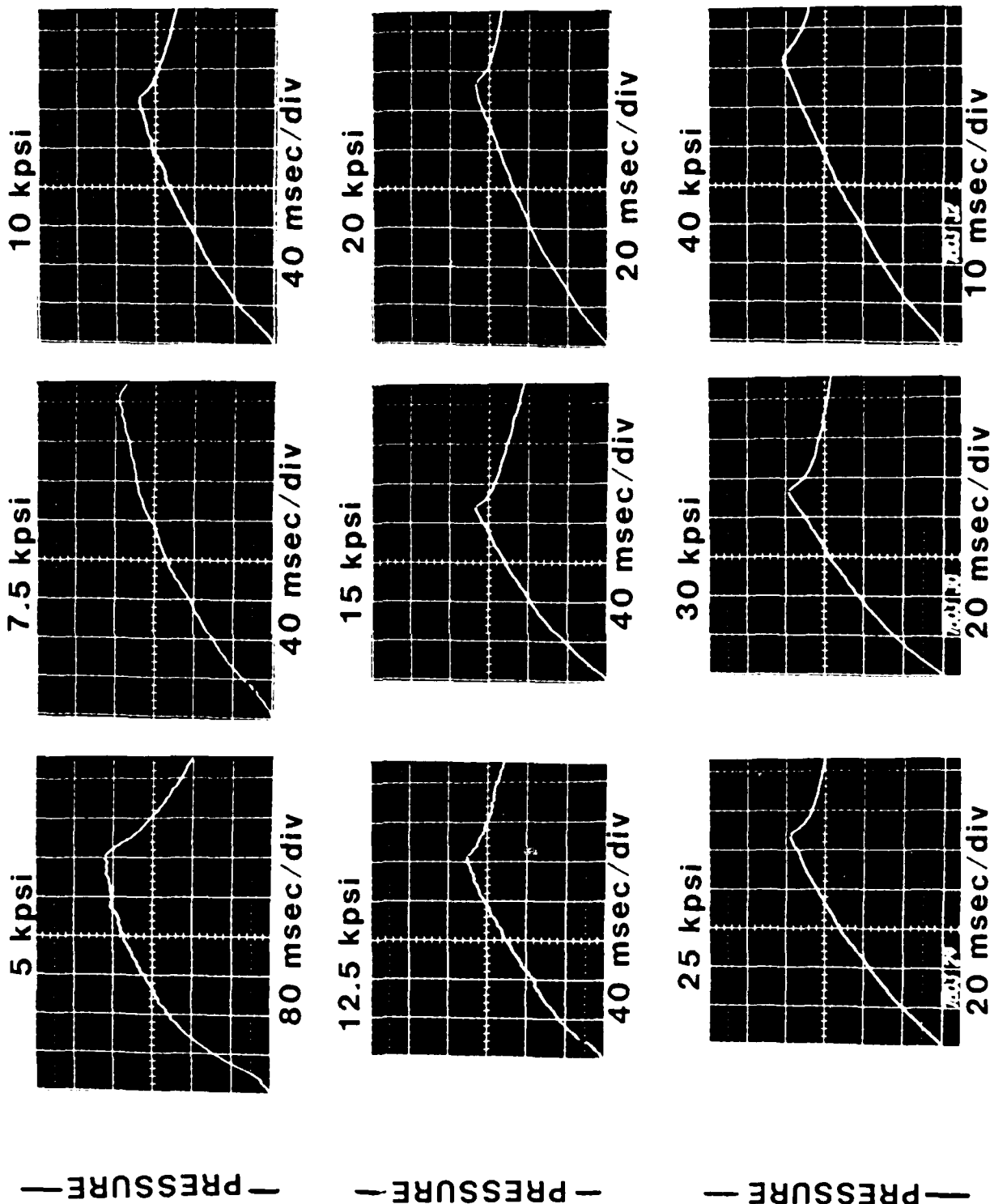
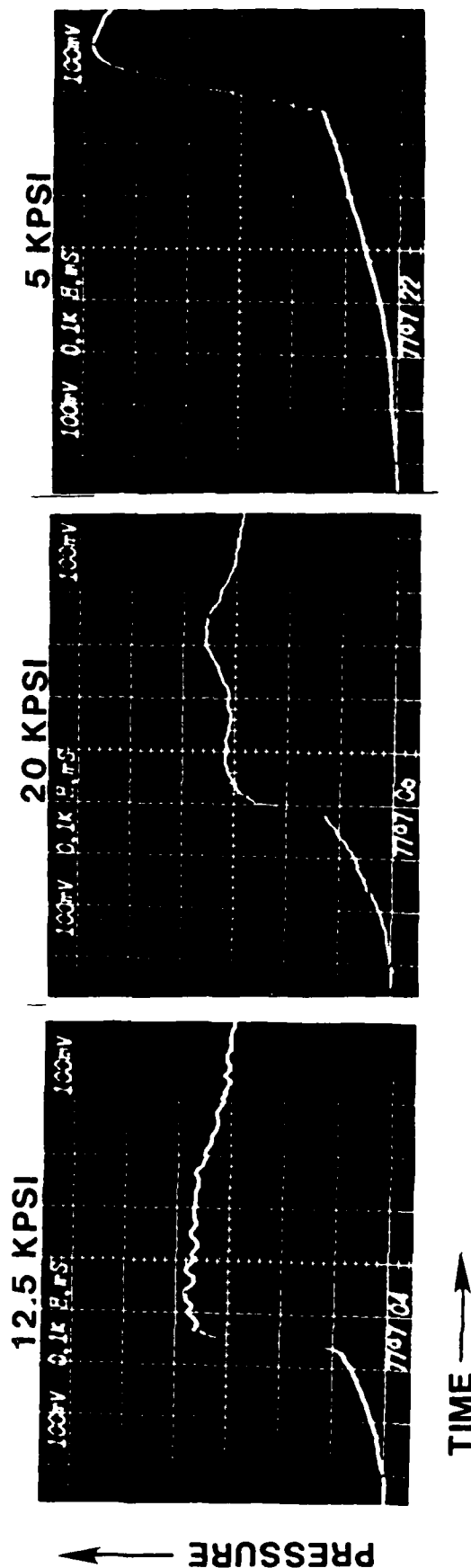


FIGURE 28.

# PRESSURE EXCURSION TECHNIQUE

25/74 PVN/RDX COMPLEX, LOT ISB 7797



TIME SCALE: 8 msec/div

PRESSURE SCALE: 100 psi/div

FIGURE 29.  
WSRL STRAND BURN RATE DATA

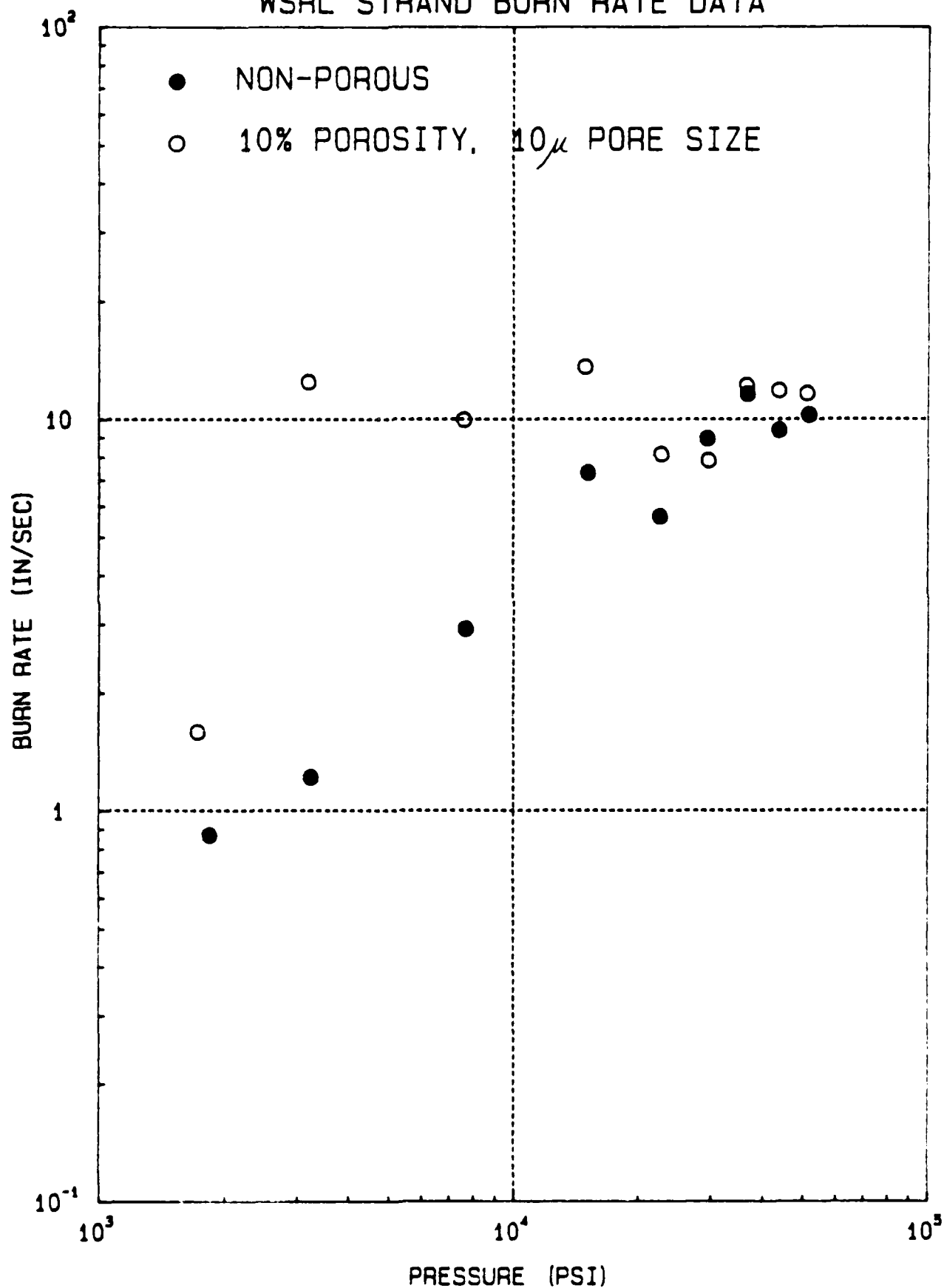


FIGURE 30.

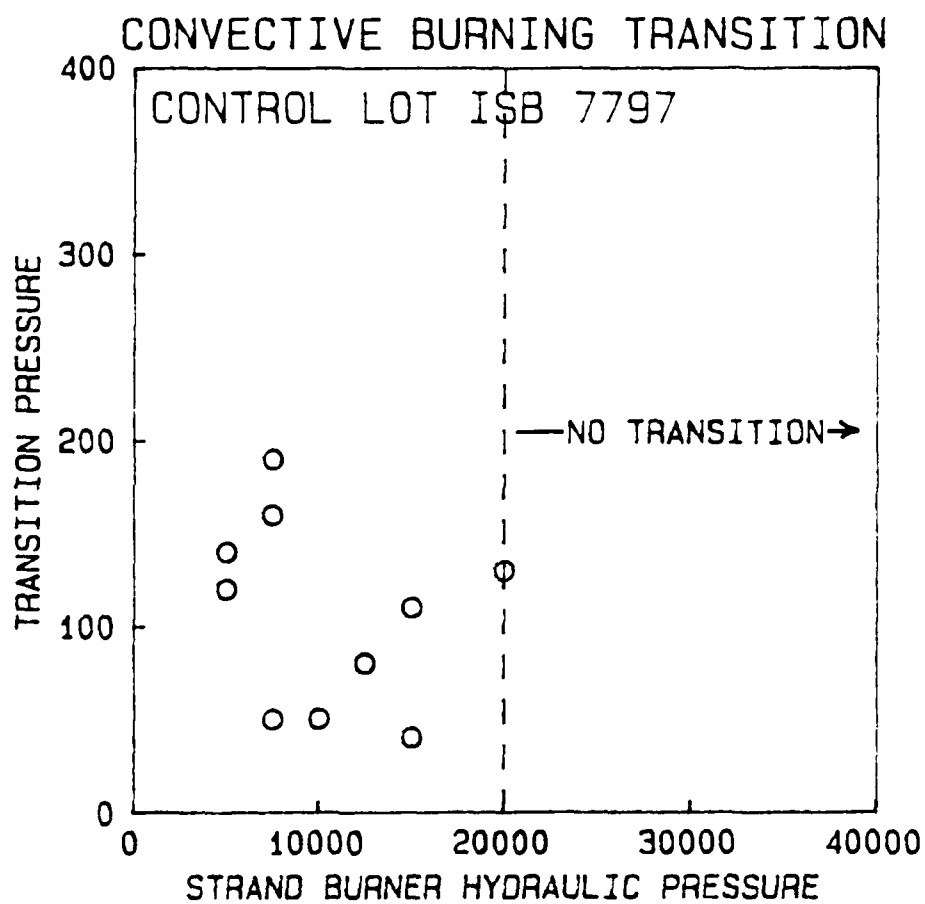


FIGURE 31.

ISB 7799: 25/74 PVN/HMX CONTROL

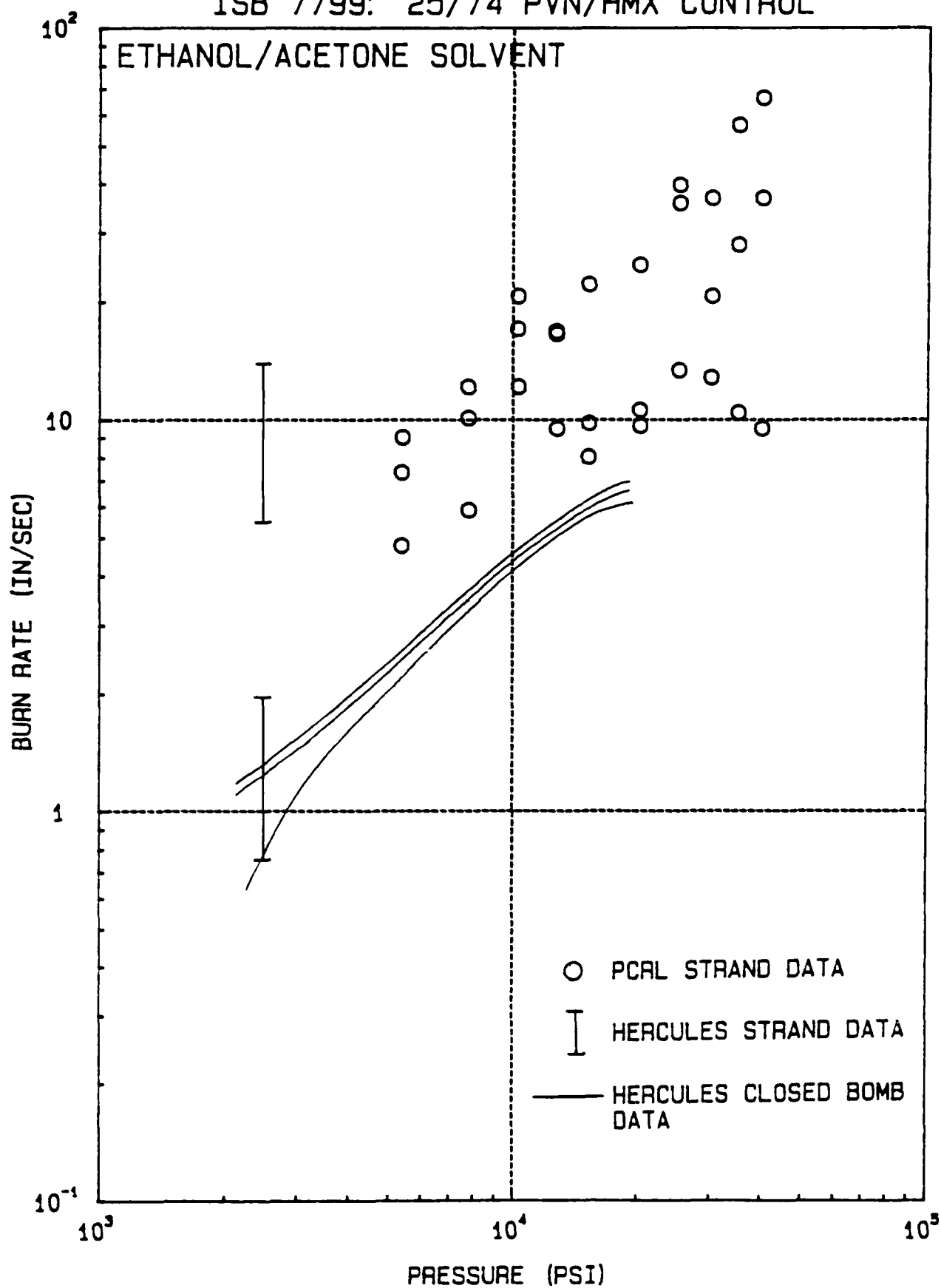


FIGURE 32.

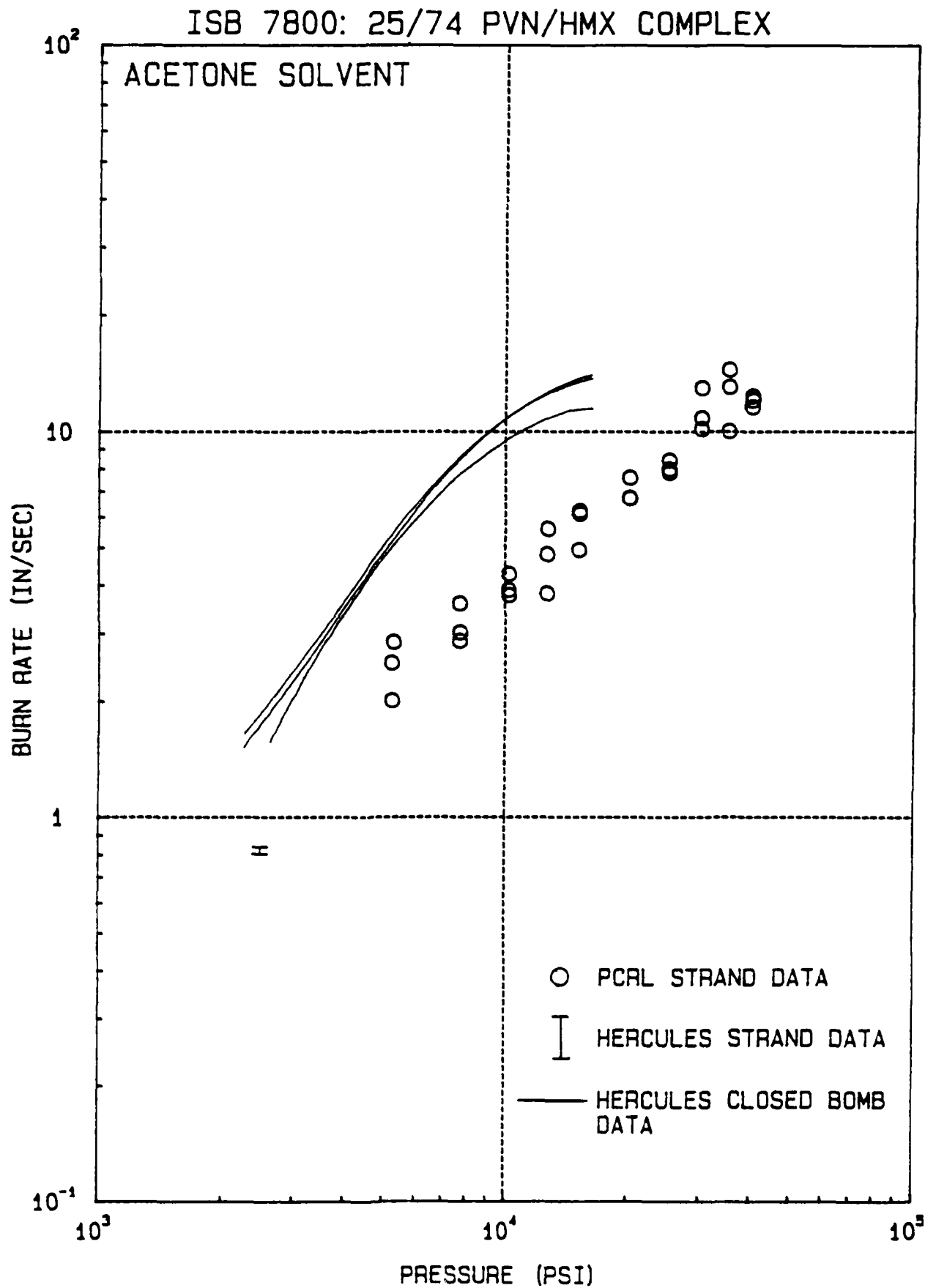




FIGURE 33.

ISB 7801: 24.5/72.5/2.0 PVN/H X/DOA COMPLEX

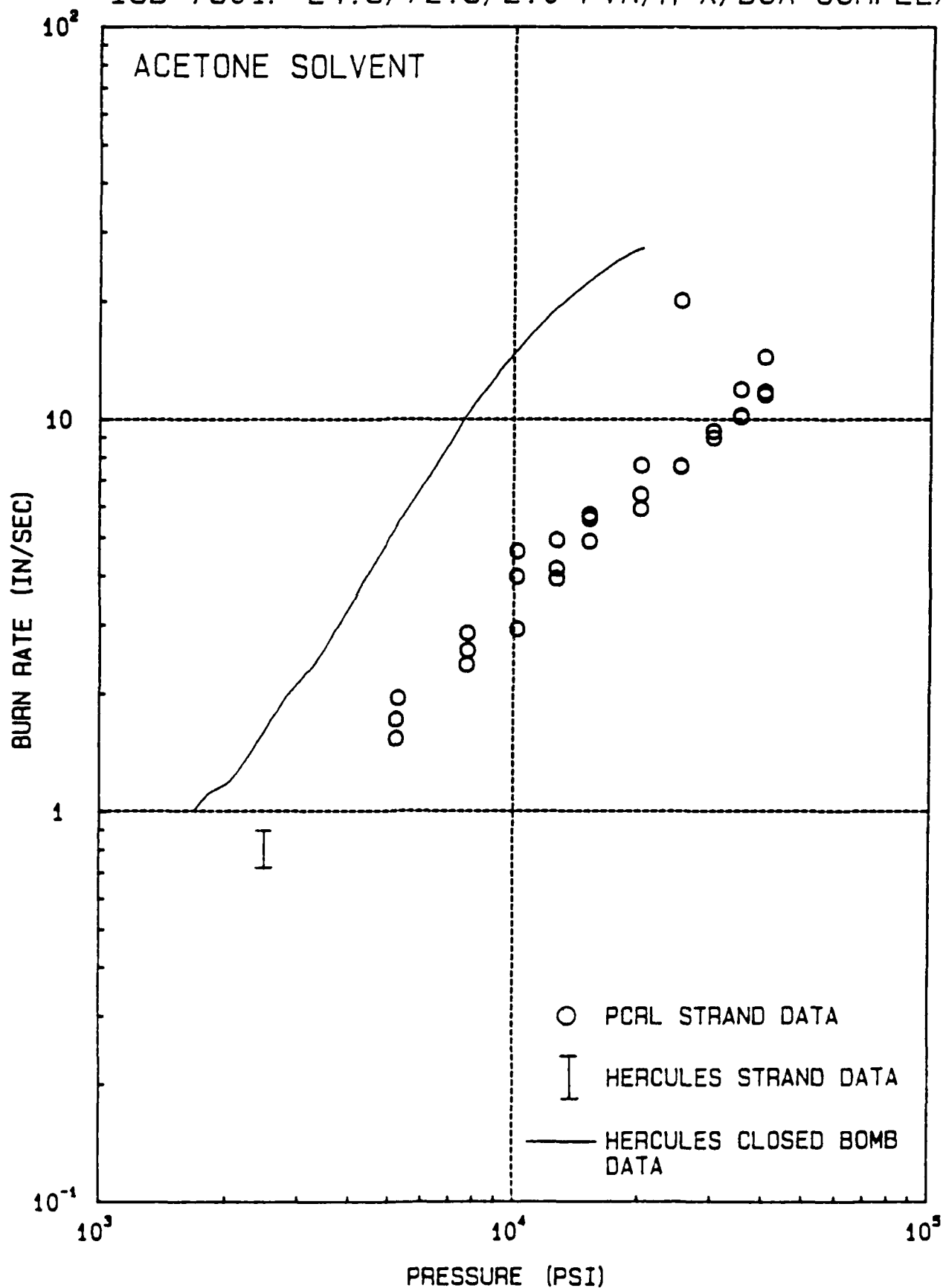


FIGURE 34.

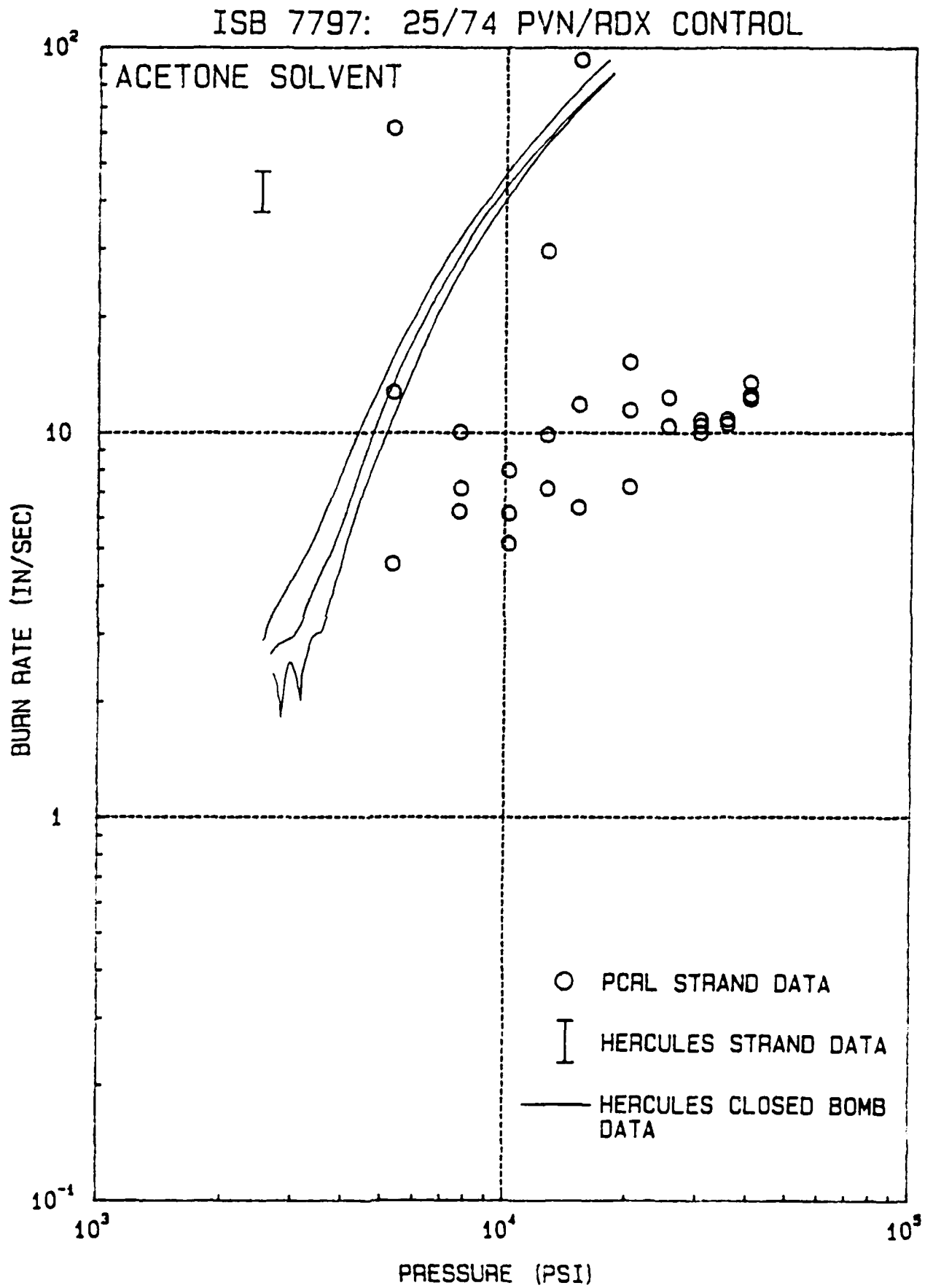


FIGURE 35.

ISB 7802: 25/74 PVN/RDX COMPLEX

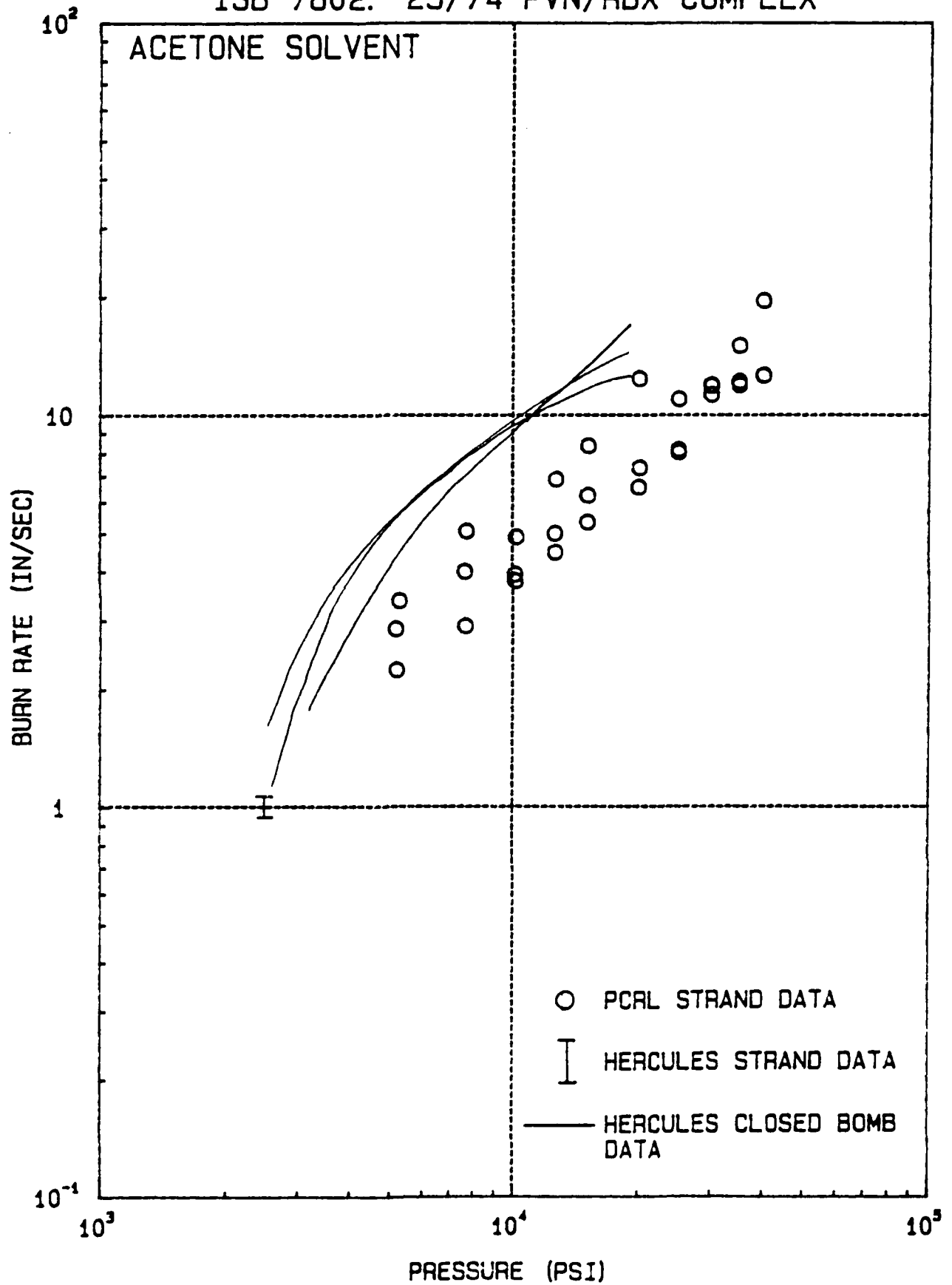


FIGURE 36.

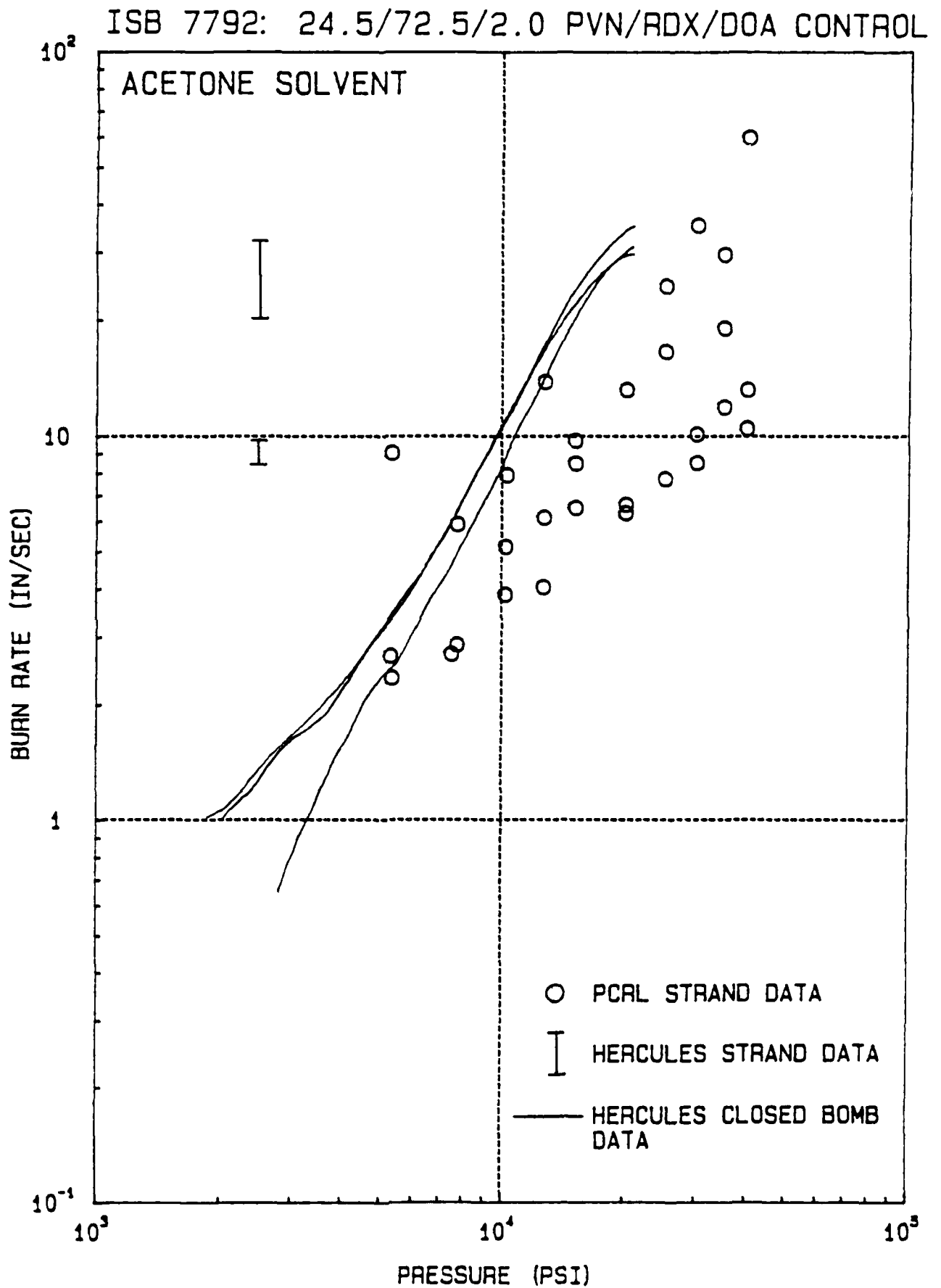
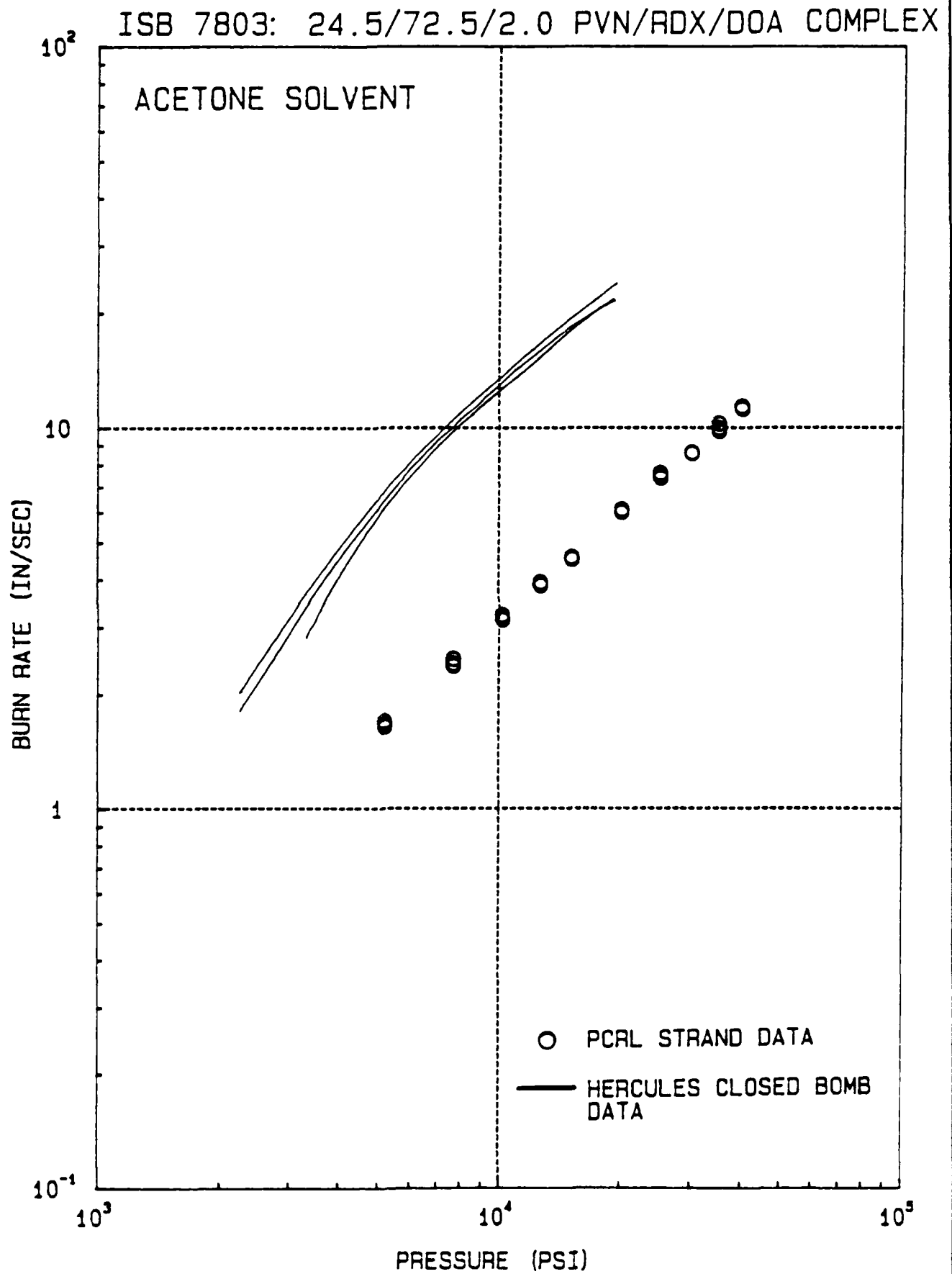


FIGURE 37.



APPENDIX

Tabulation of Strand Burn Rate Data

JA-2 LOT HCL85F003-001  
STRAND DIAMETER: 0.356"

MEAN PRESSURE (PSI)	BURN RATE (IN/SEC)
---------------------------	--------------------------

5360	1.672
5450	1.694
5420	1.687
7840	2.312
7850	2.312
7850	2.341
10300	2.904
10300	2.941
10300	2.941
12740	3.443
12780	3.504
12770	3.664
15290	4.179
15290	4.168
15270	4.261
20240	5.253
20260	5.384
20290	5.836
30250	7.860
30250	8.822
30290	8.143
40280	9.825
40280	10.103
40280	10.342

JA-2 LOT HCL85R003-001  
STRAND DIAMETER: 0.200"

MEAN PRESSURE (PSI)	BURN RATE (IN/SEC)
---------------------------	--------------------------

5275	1.609
5273	1.617
5274	1.596
7755	2.252
7759	2.385
7775	2.354
10245	3.002
10205	3.239
10228	3.141
12740	3.578
12745	3.612
12730	3.602
15243	4.271
15238	4.243
15240	4.245
20235	5.496
20238	5.513
20230	5.516
25243	6.796
25235	5.477
25238	6.797
30248	8.086
30245	8.069
30243	8.025
35248	9.200
35255	9.299
35260	9.344
40268	10.655
40263	10.707
40268	10.520

117 133 7783, 25/74:PVN/HMX CONTROL

HEBN 8131  
 49538178 8071  
 -811 111.883.

8472	8.013
8088	7.331
8580	4.784
7785	18.185
7784	10.093
7804	3.863
10088	20.833
10843	17.018
11103	12.133
12782	18.788
12733	16.543
18780	9.471
15204	22.111
18838	9.773
18213	8.013
80288	24.785
80272	3.831
80233	10.382
25213	34.852
88243	28.824
10830	12.352
10840	28.272
10813	12.303
31131	12.832
15202	17.181
28814	20.112
10118	1.412
10113	8.111
10111	10.111
10111	11.111



LOT ISB 7800, 25/74:PVN/HMX COMPLEX

MEAN PRESSURE (PSI)	BURN RATE (IN/SEC)
5255	2.514
5309	2.848
5265	2.008
7710	2.869
7725	3.583
7718	3.015
10205	3.883
10218	3.766
10217	4.269
12685	3.803
12708	5.586
12687	4.800
15195	6.215
15195	6.113
15183	4.926
20188	6.707
20185	7.586
20160	6.719
25180	7.982
25190	8.415
25175	7.815
30183	12.954
30205	10.835
30183	10.145
35198	10.016
35198	13.026
35178	14.445
40180	11.556
40205	12.033
40189	12.326

LOT 111, 24.5/72.5/2.0:PVN/HMX/DOA COMPLEX

MEAN 1.137  
STANDARD 3.112  
RSD 10.180

8017	1.031
8019	1.044
8018	1.011
7888	0.887
7787	0.877
7788	0.880
10188	0.819
10189	0.871
10202	4.808
12808	0.817
12878	4.181
12890	4.388
18180	4.837
18188	5.877
18189	5.710
20178	0.419
20180	0.309
20188	0.280
20189	0.331
20178	0.80
20188	1.141
20189	0.384
20188	0.306
20189	0.381
20188	0.211
20189	0.144
20188	0.170
20189	0.04
20188	0.0
20189	0.0

[illegible]

10017	00.777
10018	00.774
10090	00.459
10700	00.502
10703	00.503
10704	00.503
10810	00.603
10809	00.601
10802	00.510
10800	00.481
10789	00.500
10303	00.392
10170	00.680
10108	00.444
10103	00.516
00109	00.724
00100	00.583
00170	00.630
00103	00.717
00102	00.701
00108	00.710
00101	00.604
00174	00.694
00170	00.613
10170	00.450
10100	00.670
00100	00.600
00100	00.500
00100	00.400



88.74 1.00 10. 117210-  
 107.16 1.00 11  
 87892 1.00 10721. 11.12  
 8888. 1.00 11721  
 888888 1.00 11721  
 10000 1.00 11721

8848	1.008
8858	1.000
8870	8.124
7740	8.508
7740	1.008
7780	8.108
10200	1.001
10210	1.013
10220	1.001
12717	4.208
12718	4.201
12722	4.124
13128	8.488
13200	8.613
13218	4.048
20198	6.827
20208	6.488
20218	6.461
23138	6.102
23310	10.217
23318	18.281
30310	10.000
30318	11.481
30328	11.068
32210	10.287
32218	10.000
32228	18.178
40111	5.001
40112	1.000
40113	1.000



24.5/72.5/2.0:PVN/RDX/DOA CONTROL.

24.5/72.5/2.0:PVN/RDX/DOA CONTROL.

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24.5/72.5/2.0:PVN/RDX/DOA CONTROL.

24.5/72.5/2.0:PVN/RDX/DOA COMPLEX

[illegible]



END

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DTIC